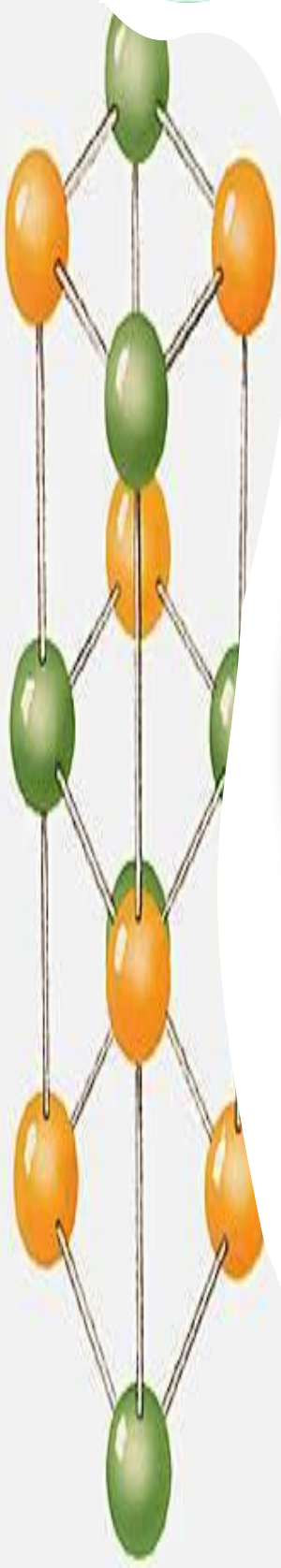
People's Democratic Republic of Algeria
Ministry of higher education and scientific research
Amar Telidji University of Laghouat

Faculty of Science

Department of Matter Science

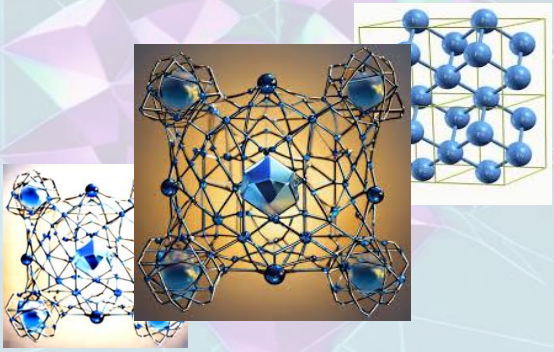


SOLID-STATE PHYSICS

Course Reminders and Exercises

Material Physics

Third year university student **L3**



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Preface

This course on solid state physics is aimed to teach the third-year university students, specializing in materials physics. The prerequisites are none other than those of general physics, statistical physics and the use of mathematical tools is simplified by providing the most useful conversion formulas. The content of this document aims to provide knowledge of the different crystalline systems of materials, enabling the identification of crystal structure using X-ray diffraction (XRD) technique.

In the first chapter, we present the models that describe the states of matter, the different point symmetry operations, and the spatial symmetry group of crystalline solids. The second chapter deals with crystal structure and the transition from the direct lattice (DL) to the indirect lattice or reciprocal lattice (RL). In Chapter 3, the interaction of X-rays with matter is discussed, where the Bragg condition must be verified. The bonds have a significant impact on the properties of materials, so in Chapter 4, we studied the different types of bonds. Finally, concluding with chapter 5 where we study the two types of lattice vibrations. We first address the photonic properties due to monoatomic chains and then diatomic chains. In this section, we will learn how to calculate and find the dispersion expression. We will also be able to calculate the total energy of a solid material and deduce the heat capacity according to the Einstein and Debye models.

Finally, teachers and relevant degree programs can find information there regarding this vast discipline that deals with the properties of materials.

Chapter I: Crystal symmetry

1.1 Introduction

The solid-state physics course in part 1 covers the various physical properties of matter in the solid state. Let's recall that the classical states of matter are classified as follows:

1. Fluid - Liquid (oil, water...)
2. Gas (O2, water vapor, N2...)
3. Solid (NaCl, glass, Pyrex...)

1.1 Classification of matter

1.1.1 Classification of the state of matter

We can classify the states of matter according to physical properties such as structural, electronic, mechanical, optical properties, etc. According to structural properties, a simple question is posed:

How is matter distributed in space in the case of air (different gases), the medium is diluted where the distance between the two patterns (particles) is much larger than the size of each of them, around 30 Å. Liquid: In the case of water (condensation of air), the distance between the patterns is of the same order of magnitude as the size of each of them. Thus, the liquid is a dense but fluid medium. Solid: example (Iron, Copper...), in this case, the distance between the patterns is too small compared to the sizes of these patterns.

1.1.2 The solid state

The solid state is not always perfect, so there is the crystalline state where the order is perfect (periodic distribution) for pure solid substances (see the periodic table), but on the other hand, there are many solids that are not crystalline, so-called "amorphous" such as glass, wood, Pyrex, and plastics.

1. In this introduction to solid-state physics, we focus only on crystalline solids for two reasons: The treatment of a crystalline

system where there is a periodic arrangement is possible compared to the amorphous state.

2. Most of the materials manufactured in thin layers are crystalline systems (multilayers, heterostructures, etc.).

1.1.3 Real crystal and perfect crystal

In reality, the perfect crystal is just a representative model of the real crystal. During the fabrication of crystals or natural crystals, there is always a certain level of impurities inside. So, for the crystal to be perfect, the impurity rate must tend towards 0 relative to the number of atoms constituting the matrix. So, in our study, we are only interested in crystals that are perfect.

1.1.4 Isotropic crystal and anisotropic crystal

We distinguish two types in the perfect crystal:

a) isotropic crystal

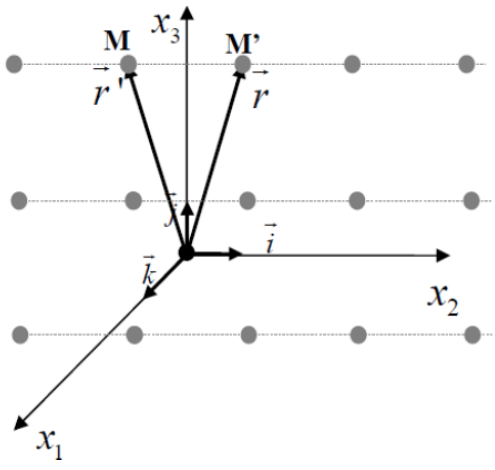
The isotropic crystal possesses the same physical properties in every direction $\overrightarrow{e_1}$, $\overrightarrow{e_2}$, $\overrightarrow{e_3}$.....therefore, the physical property is a linear combination.

b) anisotropic crystal

The anisotropic crystal possesses physical properties whose representation is matrix or tonsorial.

1.2 Transformation in the crystal space

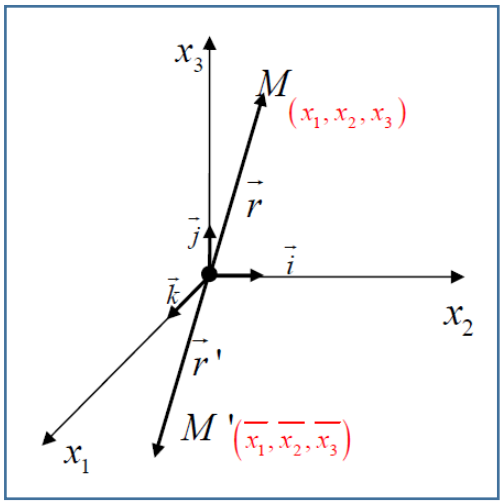
Let's consider in a solid, two points M free and O a fixed point. The distance OM - OM' between the two points M and M' remains constant.



Generally, two types of symmetrical transformations are distinguished:

Point transformation Spatial or infinite transformation

1.2.1 Point Symmetry Transformation



1.2.1.1 Inversion (I)

If each point M (x_1, x_1, x_1) corresponds to another symmetric point M' $(\overline{x_1}, \overline{x_1}, \overline{x_1})$ $\bar{1}$ or I (Herman-Maugin notation) C_i Schönflies notation)

For the matrix representation, we have: The symmetry operation (Inversion) is represented according to the dimensions.

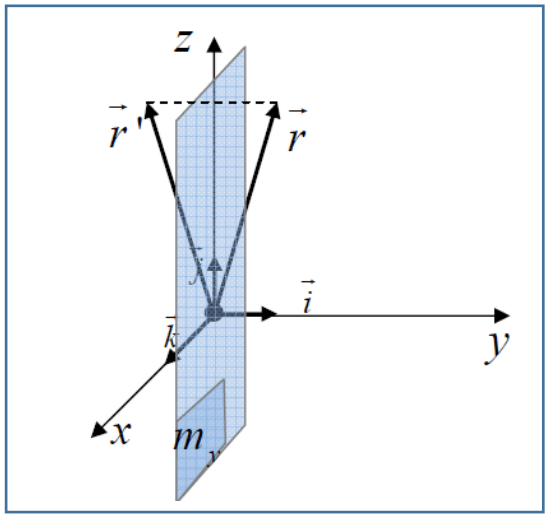
$$\vec{r} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}, \overrightarrow{r'} = \begin{pmatrix} \overline{x_1} \\ \overline{x_2} \\ \overline{x_3} \end{pmatrix} = \begin{pmatrix} -x_1 \\ -x_2 \\ -x_3 \end{pmatrix} = \begin{pmatrix} ? & ? & ? \\ ? & ? & ? \\ ? & ? & ? \end{pmatrix} . \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$$

Donc $\overrightarrow{r'} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} . \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$

Alors I=$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

1.2.1.2 Reflection (m_i) or (σ_i)

A figure possesses this symmetry if half of the figure is the mirror image of the other in a mirror or plane of symmetry.



The symbol of reflection is:

• m (Notation de Herman-Maugin)

• σ (Schönflies notation) We add a subscript before the letter σ or m to indicate the position of the mirror relative to the plane of the drawing.

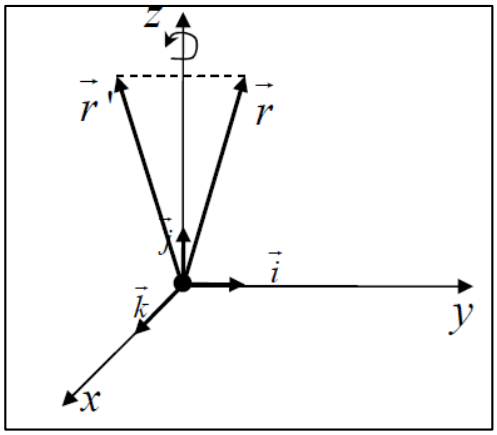
$$\vec{r} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}, \overrightarrow{r'} = \begin{pmatrix} x_1 \\ \overline{x_2} \\ x_3 \end{pmatrix} = \begin{pmatrix} x_1 \\ -x_2 \\ x_3 \end{pmatrix}, \overrightarrow{r'} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} . \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}.$$

so $m_y = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} . \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$.

Application exercise: Show that

$m_x.m_y.m_z = 1$

1.2.1.3 Rotation (n) or (Cn)



Any symmetry operation performed by rotating an angle of ($\varphi = 2\pi/n$) around a line called the axis of rotation or axis of symmetry.

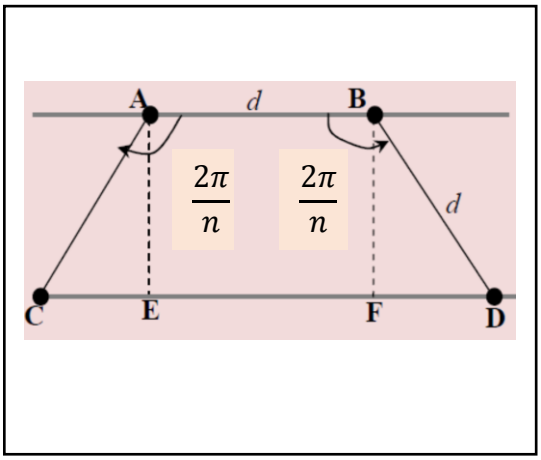
n is always an integer that represents the order of the axis of rotation.

The symbol of the rotation is:

· n: (Herman-Maugin notation)

· Cn (Schönflies notation)

The axes of rotation in solid mechanics



Let A and B be two axes of order n perpendicular to the plane of the sheet. The axis at A, acting on the one at B, brings a third one to C. Similarly, the axis at B creates a fourth one at D by rotating the same angle but in the opposite direction. By construction, the segment CD is parallel to AB. So, the distance CD must be an integer multiple of AB.

$\left\{ \begin{matrix} CD = m.AB \\ CD = 2ABsin\left(\frac{2\pi}{n} - \frac{\pi}{2}\right) + AB \end{matrix} \right\} \rightarrow 2cos\left(\frac{2\pi}{n}\right) = 1 - m$ The rotations An compatible with the periodicity therefore correspond to the allowed values of m given by this equation. There are 5 of them:

M	Cos α	a	$n = \frac{2\pi}{a}$
-1	1	π	2
0	1/2	$\frac{2\pi}{3}$	3
1	0	$\frac{\pi}{2}$	4
2	-1/2	$\frac{\pi}{3}$	6
3	**-1**	2π	**1**

So, n=1, 2, 3, 4, 6

The notation of the rotation axis according to:

•Herman-Maugin notation: n = 1, 2, 3, 4, 6

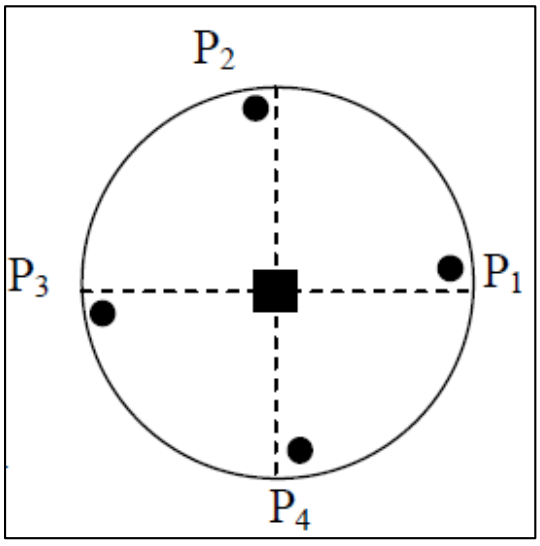
• Schönflies notation: C_1, C_2, C_3, C_4, C_6.

Note:

The axis of rotation is represented by C_n, but the symmetry operation is represented by C_n^p where p represents the number of images.

Example

$$\varphi = \frac{\pi}{2} \rightarrow n = \frac{2\pi}{\varphi = \frac{\pi}{2}} \rightarrow n = 4$$



So, according to the C4 axis of symmetry, we obtained 04 equivalent images. The images are: C_4^1, C_4^2, C_4^3, C_4^4.

We notice that the operation C_4^2 is equivalent to C_4^1 by simplifying n and p. Also, C_4^4 and E are the same.

b) Graphical representation and symbol

Ordre de l'axe de rotation	Représentation graphique		Terminologie
	Perpendiculaire au plan de dessin (⊥)	Parallèle au plan de dessin (||)	
1			-
2			Axe binaire
3			Axe ternaire
4			Axe quaternaire
5			Axe quinaire
6			Axe sénaire

c) Matrix representation of rotation:

The matrix representation of the axis of rotation is given by:

1. The direction carrying the axis of rotation.
2. The angle of rotation.

Example:

$\left\{\begin{matrix}1- \text{ Sens vers XOX}' \\ 2- L'angle\ \varphi = \frac{\pi}{3}\end{matrix}\right\} \Longrightarrow$ so the axis of rotation is written as: 6_x or C_{6x}

We represent below the matrices of the axes of symmetry according to the three directions Ox, Oy, and OZ.

Axe de rotation selon ***OX***	Axe de rotation selon ***Oy***	Axe de rotation selon ***Oz***
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{pmatrix}$	$\begin{pmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{pmatrix}$	$\begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$

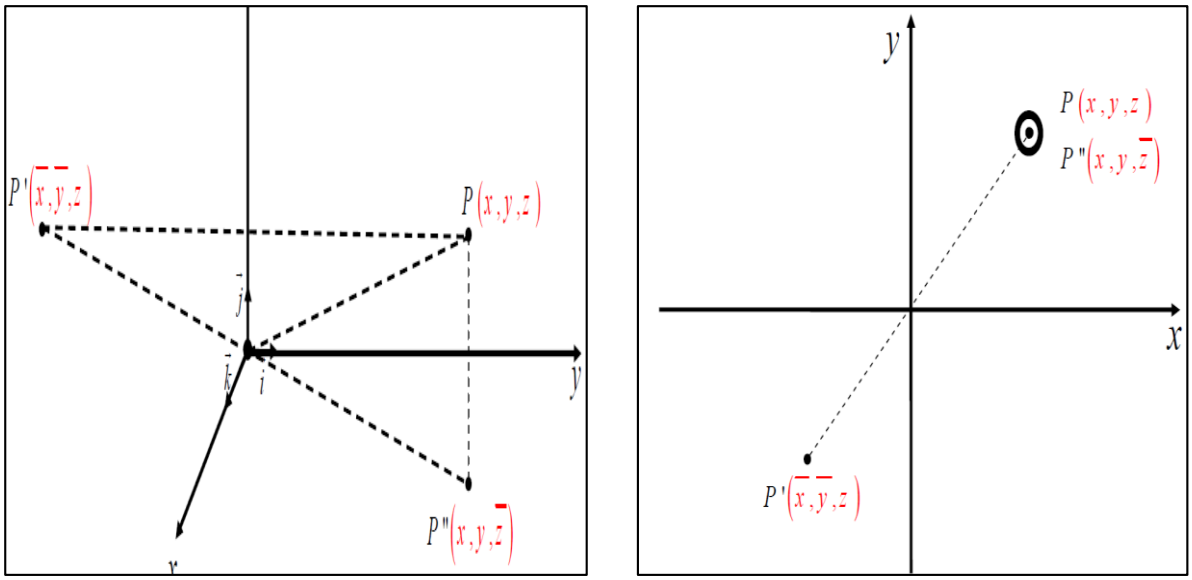
1.3 Composite Point Transformations

1.3.1 Inversion –rotation

Operation consists of a rotation of $2\pi/n$ followed by an inversion whose center I is located on the axis of rotation. The resulting element is called an "inversion axis."

The roto-inversion of order n is denoted $\bar{n}$ (Herman-Maugin notation) or S (Schönflies notation).

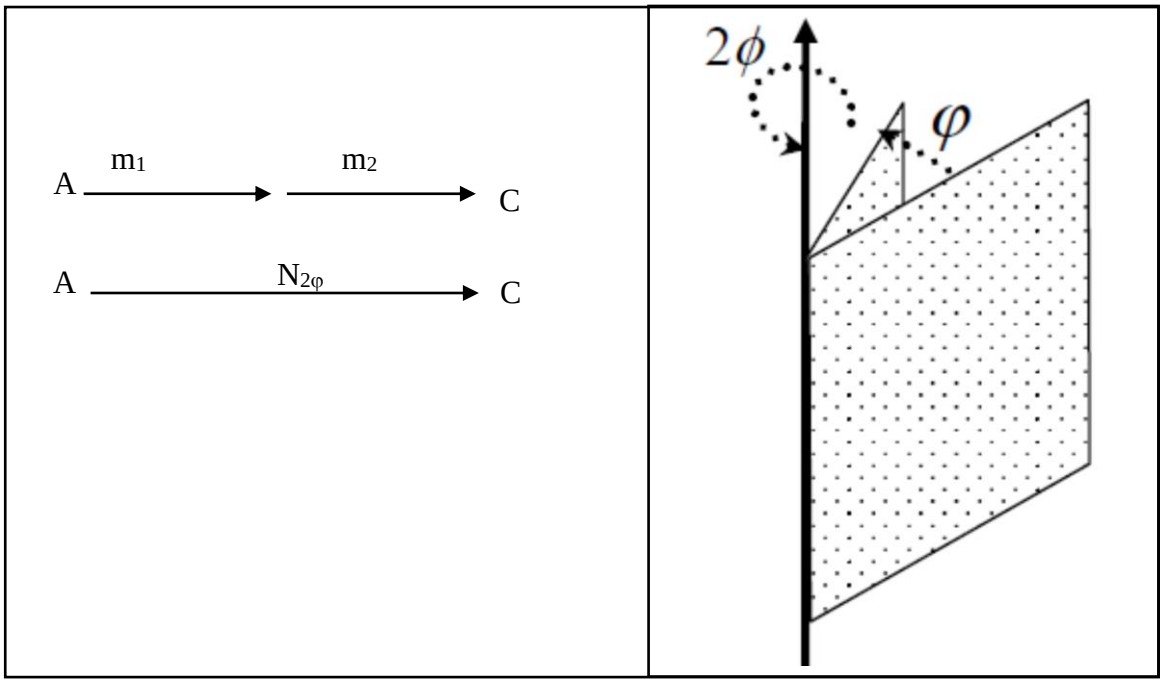
Example 2:



1.4 Theorems of Crystal Symmetry

1.4.1 Theorem 1

The line of intersection of two mirrors is always an axis of symmetry at an angle of rotation double the angle formed by the two mirrors.



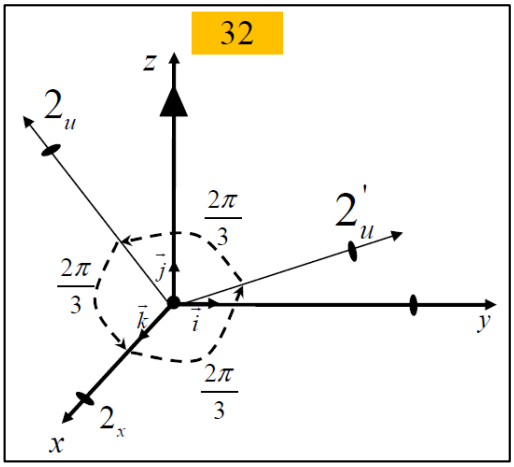
Note

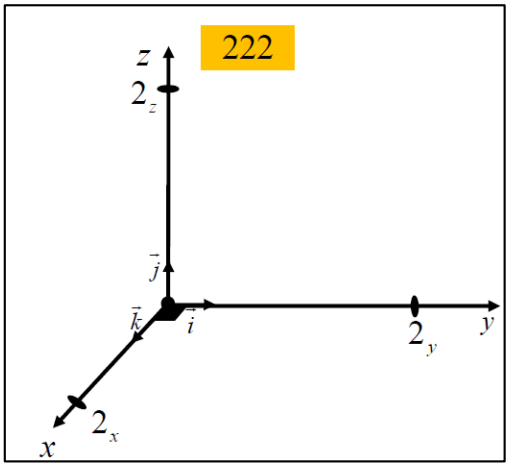
Similarly with mirrors, the product of two rotations results in a rotation.

1.4.2 Theorem 2

If an axis of order n is perpendicular to an axis of order 2, then there are n axes of order 2 perpendicular to the axis of order n. The combination of the symmetry axis of order n and the axis of order 2 that is perpendicular to it is denoted n2 such that: 32, 222, 42

Example





1.4.3 Theorem 3

a. The intersection product of an even symmetry axis with a mirror that is perpendicular to it is a center of symmetry. The combination of the even symmetry axis and order n with a mirror that is perpendicular to it is denoted as n/m.

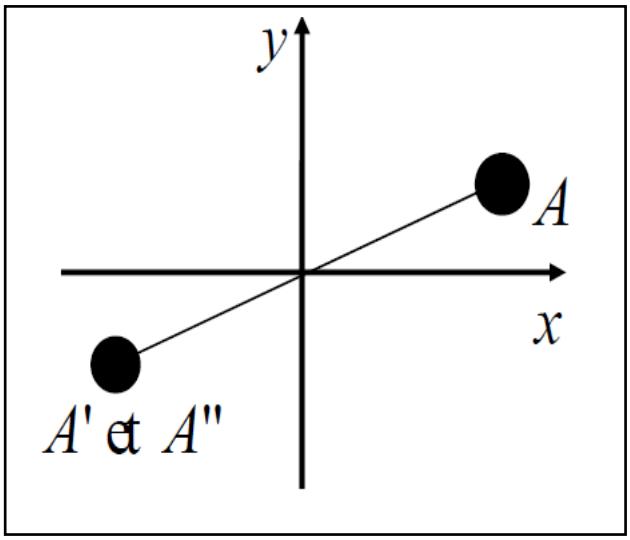
b. If an even-order axis of symmetry contains a center of symmetry, then this axis also has a mirror that is perpendicular to it.

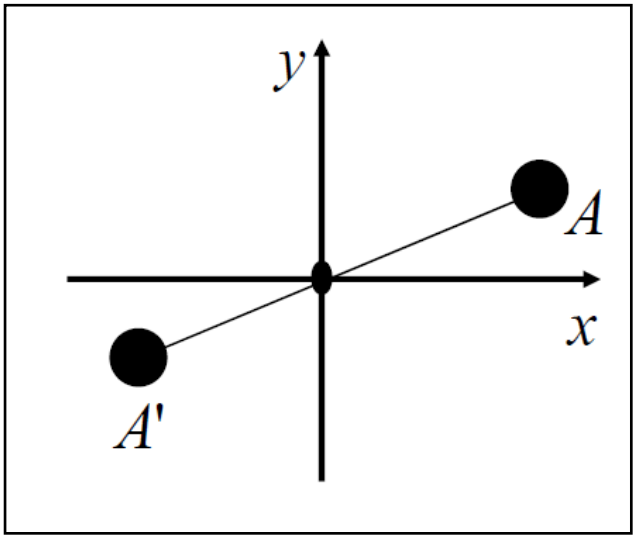
c. If a mirror passes through a center of symmetry, then it passes through this center perpendicularly to the mirror, an axis of symmetry of even order.

Example: Show graphically and analytically the following relationship: $\bar{1}.m_z = 2_z$.

1) Graphically

$$A \xrightarrow{\overline{(1)}} A' \xrightarrow{m_Z} A''$$





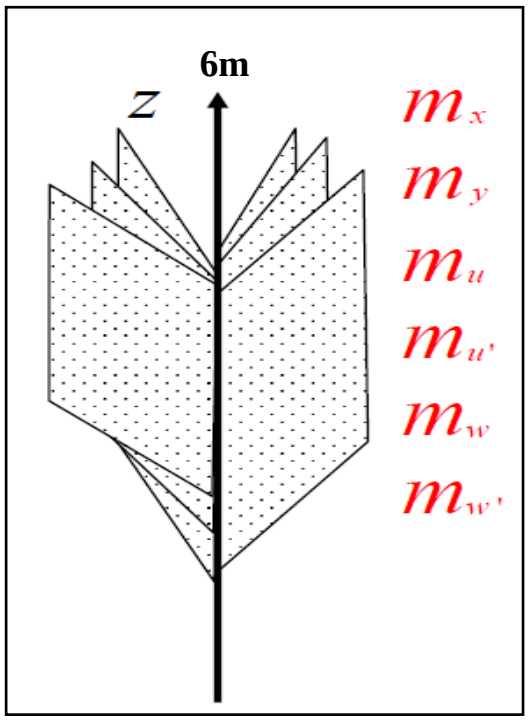
2) Analytically

$$\bar{1}.m_z = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = 2_z$$

1.4.4 Theorem 4

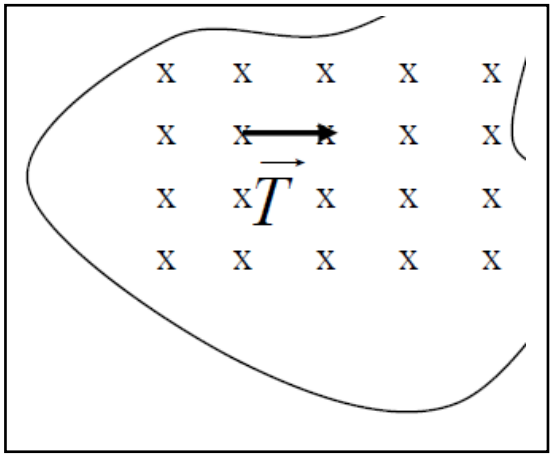
If along an axis of symmetry of order n there is a mirror (plane of symmetry), then there are n mirrors that are parallel to the main axis. This combination gives rise to a notation of nm.

Example



1.5 Infinite (spatial) symmetry transformations

1.5.1 Pure Translation ($\vec{T}$)



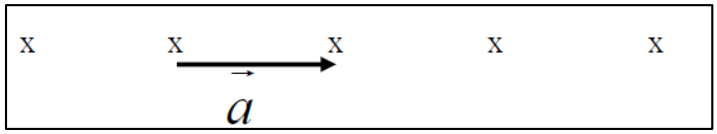
Pure translation is a symmetry operation, so when the point M moves from the origin to the end of a vector, it brings point M'. Infinite + periodic object the value x of the small possible translation is called the period.

Pure translation is a symmetry operation, so when the point M moves from the origin to the end of a vector, it brings point M'.

- Infinite + periodic object
- The value x of the small possible translation is called the period.

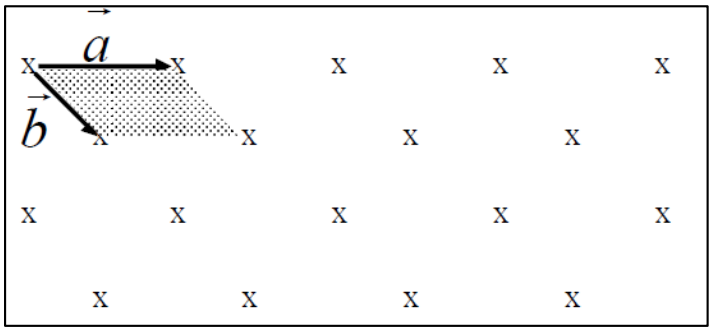
Representation at (1D)

$$\vec{T} = n\vec{a}$$



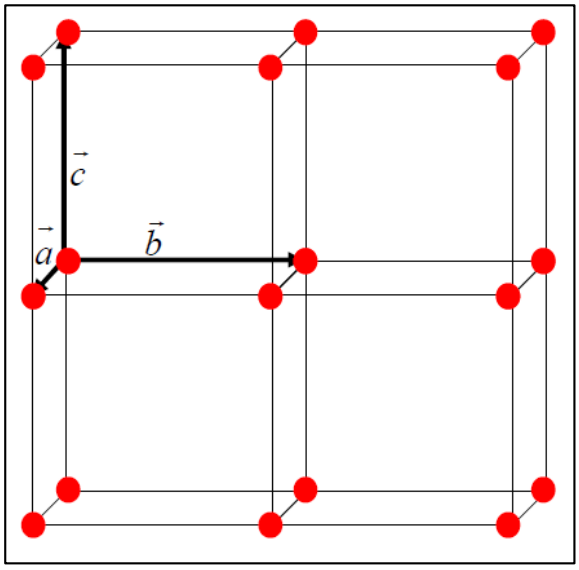
Representation at (2D)

$$\vec{T} = n\vec{a} + m\vec{b}$$



Representation at (3D)

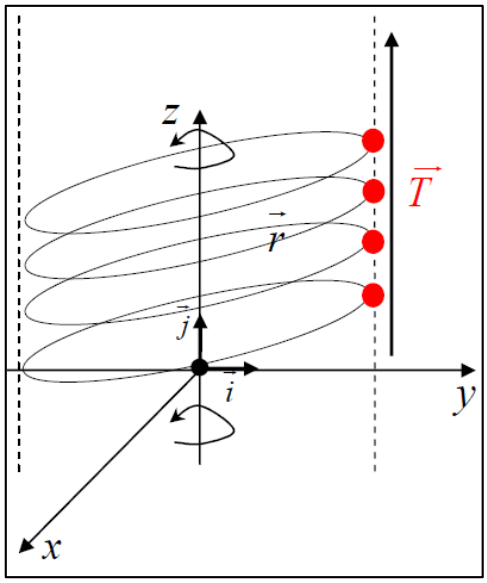
$$\vec{T} = n\vec{a} + m\vec{b} + p\vec{c}$$



Such that n, m, and p are integers $\mathbb{Z}$.

1.5.2 Helical Axis (Translation + Rotation)

It is a rotation of $2\pi/n$ around an axis necessarily followed by a translation $\vec{T}$parallel to the axis of rotation.



A helical axis is represented by the symbol:

2_1,

3_1, 3_2

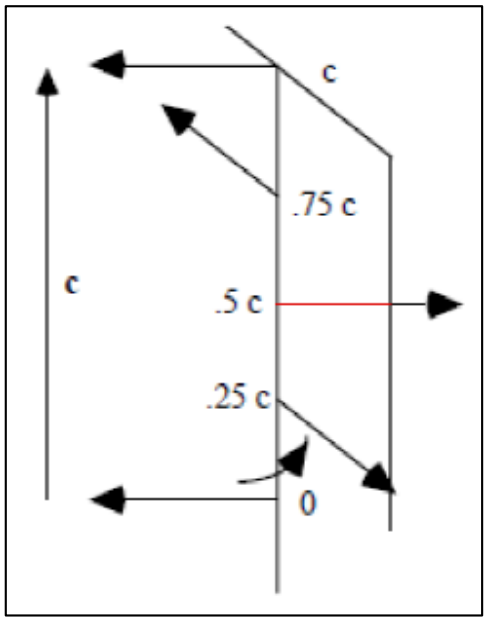
4_1, 4_2, 4_3

6_1, 6_2, 6_3, 6_4, 6_5

So, there are 11 allowed helical rotations.

Example 4_1

We show a helical axis 4_1: the symmetry operation is a 90° rotation followed by a translation of ¼ of the fundamental translation vector parallel to the axis of rotation, that is, c/4.



The helical axis 42 is characterized by the succession of a 90° rotation and a translation of c/2.

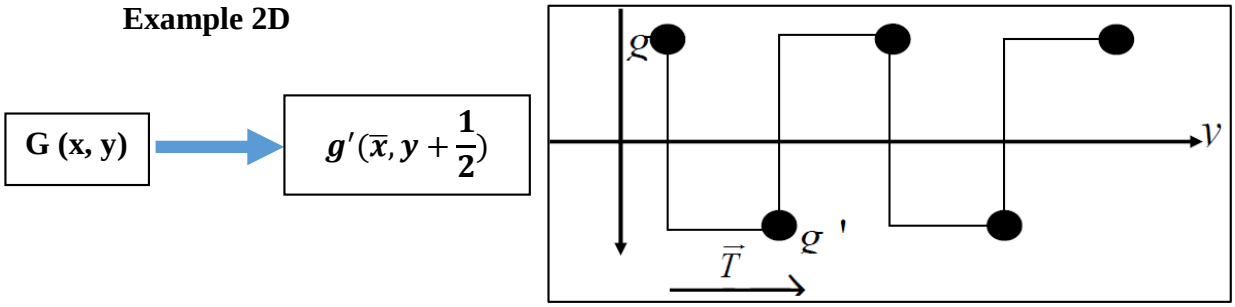
1.5.3 Slip Plane (Translation + Reflection)

A helical rotation is a composite operation. A slip plane and a translation of a fraction of an elementary translation. Different types of slip planes are distinguished according to the orientation of the translation relative to the plane.

When the translation is parallel to the slip plane and equal to half of a translation vector of the lattice, we have an axial slip plane. Depending on whether the translation is parallel to vector a, b, or c, it will be referred to as a slip a, b, or c. (a-glide, b-glide...).

When the translation does not occur parallel to the plane, we have a diagonal slip plane(n-glide).

Example 2D



The existing slip plans:

a: $\vec{T} = \frac{\vec{a}}{2}, \vec{T} = \frac{\vec{b}}{2}, \vec{T} = \frac{\vec{c}}{2}$.

n: $\vec{T} = \frac{\vec{a}+\vec{b}}{2}, \vec{T} = \frac{\vec{a}+\vec{c}}{2}, \vec{T} = \frac{\vec{b}+\vec{c}}{2}$

d: $\vec{T} = \frac{\vec{a}\mp\vec{b}}{2}, \vec{T} = \frac{\vec{a}\mp\vec{c}}{2}, \vec{T} = \frac{\vec{b}\mp\vec{c}}{2}$

1.5.4 Inversion and translation

Inversion and translation are not new symmetry operations since they amount to a simple inversion by a displaced center.

$$g(x, y, z) \xrightarrow[\text{Translation}]{\text{Inversion}} g'(\bar{x} + \frac{1}{2}, \bar{y}, \bar{z})$$

So, the inversion moves from **g (0, 0, 0)** ⟶ **g' (1/2, 0, 0)**

1.6 Stereographic Projection

Stereographic projection allows for the representation of any point located on a sphere in a projection plane. The stereographic projection is essentially used for the representation of the symmetry elements of a crystal.

1.7 Point group of symmetry:

In solid-state physics, when a figure possesses one or more elements of symmetry, it is said to have a symmetry group in the mathematical sense.

1.7.1 Definition

A set G containing the elements g_i is called a group when the following conditions are met:

- **Internal operation:**

The operation used between the elements g_i is always an internal operation, therefore:

$$\forall \boldsymbol{g_i, g_j} \in \boldsymbol{G}, \boldsymbol{g_i} \otimes \boldsymbol{g_j}, \boldsymbol{g_j} \otimes \boldsymbol{g_i} \in \boldsymbol{G}$$

- **Associative operation**
- **The operation used is associative, therefore**:

$$\forall \boldsymbol{g_i, g_j, g_k} \in \boldsymbol{G}, \boldsymbol{g_i} \otimes \left(\boldsymbol{g_j} \otimes \boldsymbol{g_k} \right) = \left(\boldsymbol{g_i} \otimes \boldsymbol{g_j} \right) \otimes \boldsymbol{g_k}$$

- **Neutral element**

The set contains a single and unique neutral element, therefore:

$$\forall \boldsymbol{e, g_i} \in \boldsymbol{G}, \boldsymbol{g_i} \otimes \ \boldsymbol{e} = \boldsymbol{e} \otimes \ \boldsymbol{g_i} = \boldsymbol{g_i}$$

- **Symmetric element**

The set assigns to each element gi a single and unique symmetry element g_j, such that:

$$\forall \boldsymbol{g_i, g_j} \in \boldsymbol{G}, \boldsymbol{g_i} \otimes \boldsymbol{g_j}, \boldsymbol{g_j} \otimes \boldsymbol{g_i} = \boldsymbol{e}$$

Examples:

Each symmetry element itself forms a group with these symmetry operations such that

$$C_2 = \{C_2^1, C_2^2\} = \{C_2^1, C_2^2\}$$

$$C_{\bar{1}} = \{\bar{1}, (\bar{1})^2\}$$

$$m = \{m, m^2\} = \{m, E\}$$

Note:

The number i of elements of group G such that gi and i are finite or infinite is called the order of the group.

Example: $G = \{x, y, z, E\}$ donc ***i=4.***

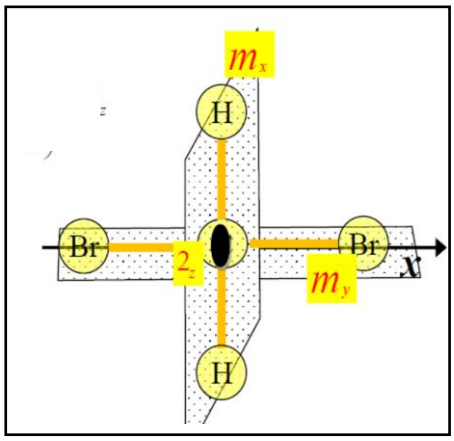
So, there are two mirrors m_x and m_y and an order 2 axis along the OZ axis.

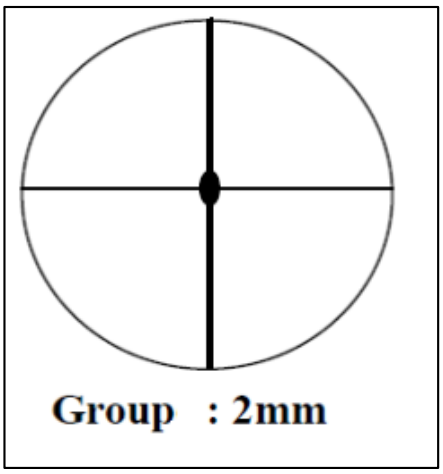
$$\boldsymbol{2mm = C_{2v} = \{C_2^1 = m_x, m_y, E\}}$$

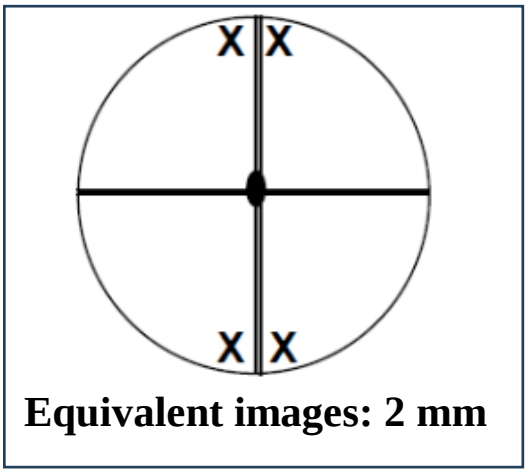
So,

$$m_x.m_y = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 2_z$$

$\otimes$	E	C_2^1	m_x	m_y
E	E	C_2^1	m_x	m_y
C_2^1	C_2^1	E	m_y	m_x
m_x	m_x	m_y	E	C_2^1
m_y	m_y	m_x	C_2^1	E







1.8 Some special groups

1.8.1 Cyclic Group C_n

The group generated by a symmetry element that is composed of powers of an operation p = 1, 2, 3……. is called a cyclic group.

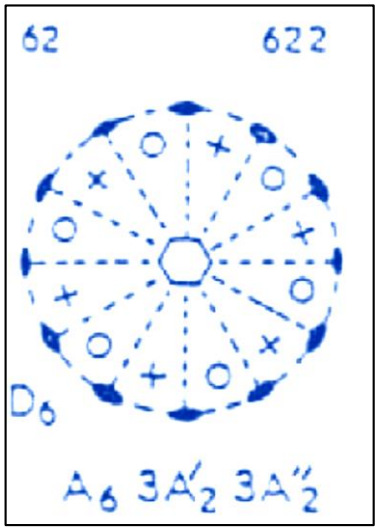
Example C_6:

$$C_6 = \{C_6^1, C_6^2, C_6^3, C_6^4, C_6^5, C_6^6\} = \{C_6^1, C_3^1, C_2^1, C_6^4, C_6^5, E\}$$

1.8.2 Double group D_n

It contains an axis of order n and n axes of order 2 perpendicular to the main axis.

Example: D_6



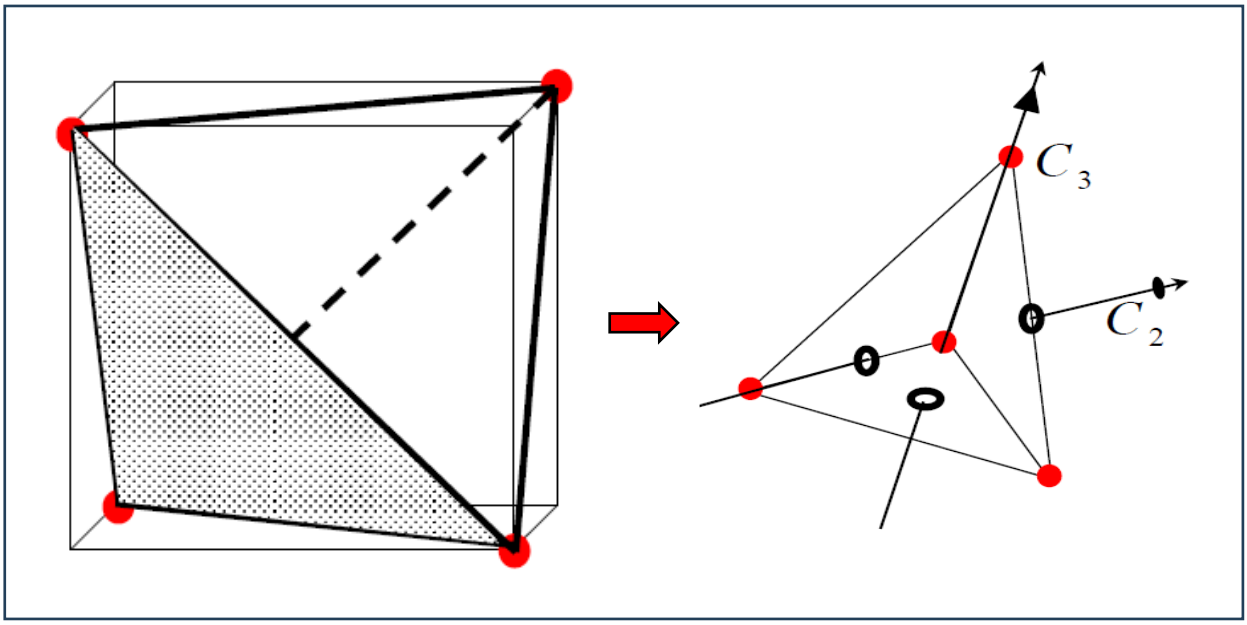
1.9 Point Symmetry Groups in 3D

We classify the symmetry groups in 3D according to the different combinations. Groups that possess multiple axes of rotation (T et O)

1.9.1 Group 23 (T: Tetrahedron)

It is a tetrahedral group formed by the intersection of 4 planes and which contains:

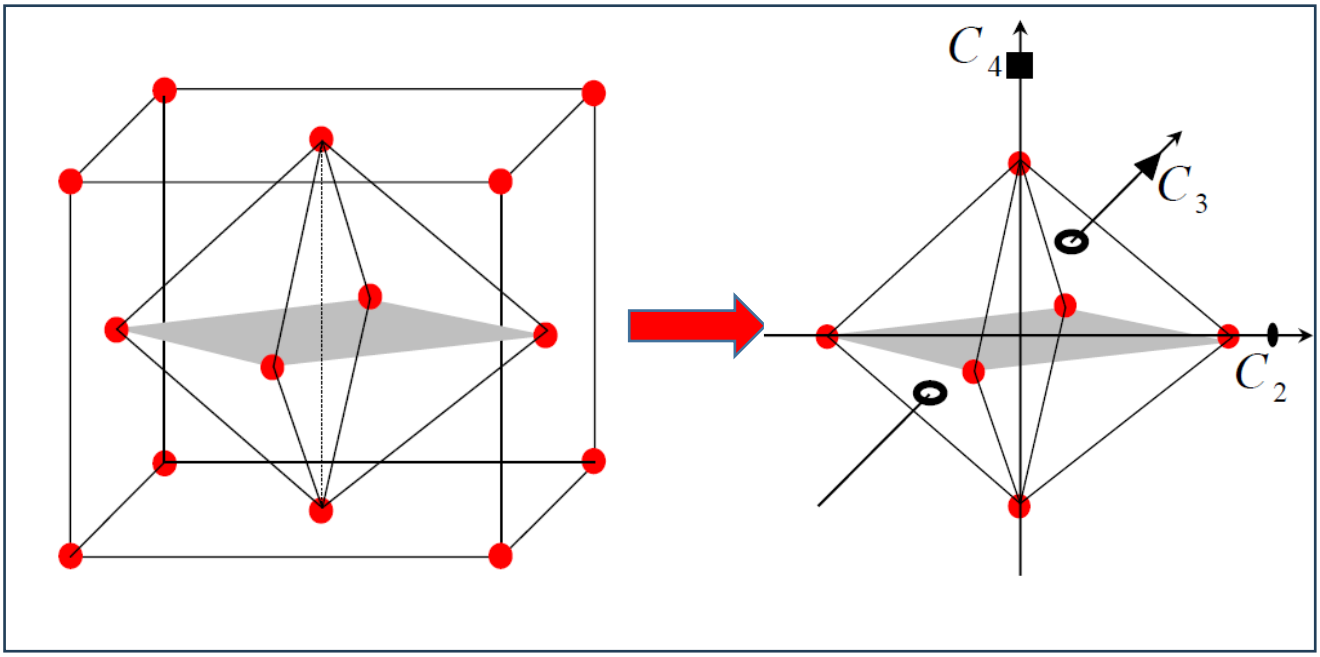
- **4 axes of order 3**
- **3 axes of order 2**



1.9.2 Group 432 (O)

This group is found in the face-centered cubic structure. The octahedral group or O contains:

- axes of order 4
- axes of order 3
- 6 axes of order 2



Note:

When other symmetry elements are added to the T or O groups, other space groups are obtained.

1.9.3 Space group:

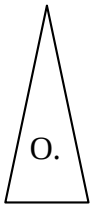
We know that the point symmetry groups represent only a subset of all the possible operations that can be found in crystalline structures.

Space groups contain more than just point elements; the translation $\overrightarrow{T}$ gives us an infinite number of groups, but we limit ourselves to 230 groups that are of interest in solid-state physics.

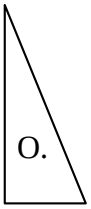
Series Nº 01: Crystal symmetry

Exercise 01

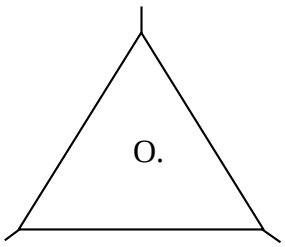
Let the following plane geometric figures be:



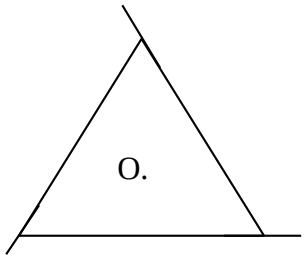
(01)



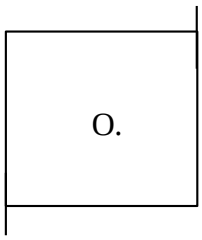
(02)



(03)



(04)



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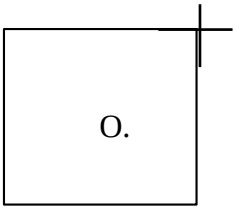

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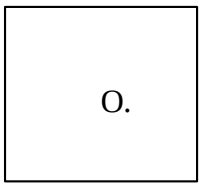

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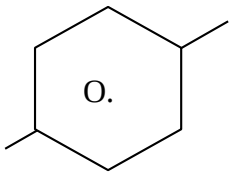
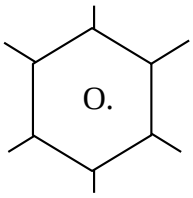
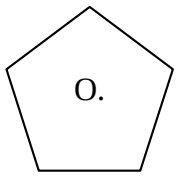


(08)



(09)



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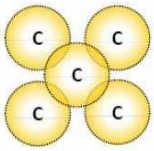

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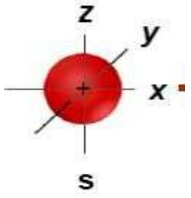

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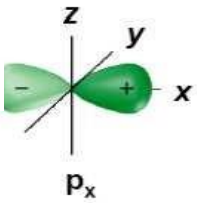

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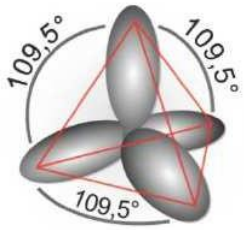

(14)

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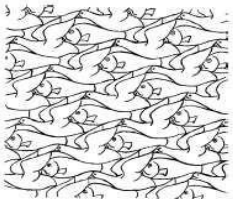

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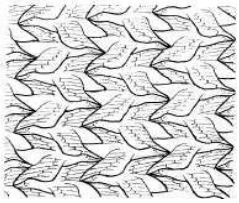

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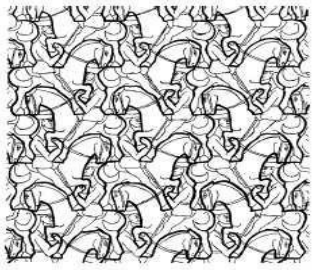

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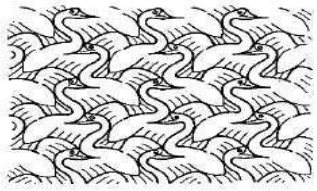
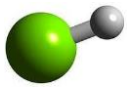


(19)

- Find the equivalent figures and their number of the figures above obtained by rotation transformation around an axis passing through O and perpendicular to the plane of the figures.
- Determine the planes of symmetry.

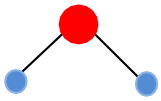
Exercise 02

We are given the following molecular structures:

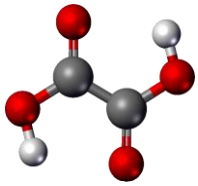


HCl

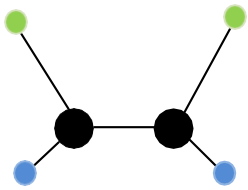
CO_2



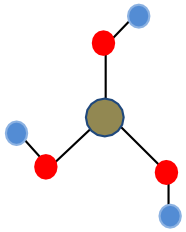
H_2O



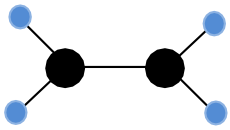
$C_2H_2O_4$



$C_2H_2Cl_2$

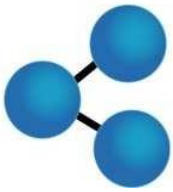


H_3BO_3

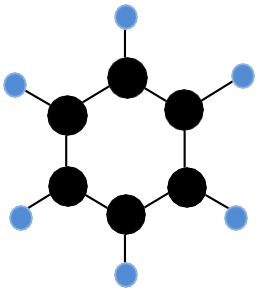


C_2H_4

CH_4



O_3



C_6H_6

- Find the elements of symmetry.
- Provide their two- dimensional representation on the XOY plane.

Exercise 03

1. Show graphically and analytically (matrices) that $\overline{A_2} = m$

2. Verify the following relationships: $\overline{A_n} = A_n.C$ As such (n = 2, 3, 4, 6).

3. Find the symmetry transformation operation equivalent to the composed transformation:

$\sigma.A.\sigma^{-1}$ as such ($\sigma = m_x$ and $n = 2, 3, 4, 6$)

Exercise 04

- Show that the elements of the sets E1, E2, and E3 form symmetry groups.

- Provide the symmetry group corresponding to the sets E1, E2, and E3.

$$E_1: C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad C_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$E_2: C_4 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} C_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} C_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$E_3: C_4 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} C_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} C_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} C_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Exercise 05

1.We provide the multiplication tables of the sets below. Verify that the elements of the sets E1, E2, E3, E4, E5, and E6 form symmetry groups.

E1

	a
a	a

E2

	a	b
a	a	b
b	b	a

E3

	a	b	c	d
a	b	d	a	c
b	a	c	b	a
c	a	b	c	d
d	c	a	d	d

E4

	a	b	c	d
a	b	d	a	c
b	a	c	e	a
c	a	b	c	d
d	c	a	d	d

E5

	a	b	c	d
a	a	b	c	d
b	b	a	d	c
c	c	d	a	b
d	d	c	b	a

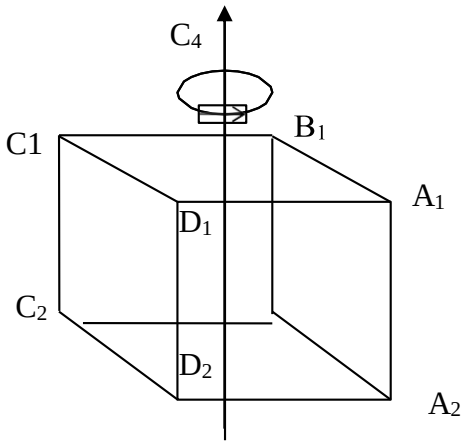
E6

	a	b	c	d	e	f
a	b	e	a	f	d	c
b	f	d	b	c	a	e
c	a	b	c	d	e	f
d	e	c	d	b	f	a
e	c	f	e	a	b	d
f	d	a	f	e	c	b

2. Give the symmetry group that corresponds to tables E1, E2, and E5 if the latter are groups.

Exercise 06

Determine the transformation matrices in a rectangular axis system for the $\overline{2}_z$ symmetry element and the 3_z symmetry element in a hexagonal axis system.



Exercise 07

We assume the crystalline structure is represented in four axes O_x, O_y, O_z, and O_u.

Show that: $2_x . 3_z = 2_u$ and $2_z . 3_x = 2_y$

Exercise 08

Find the symmetry elements of the C_{2v}, C_{3v}, C_{2h}, C_{4h} groups. Give their two-dimensional representation.

Exercise 09

Provide the set of operations of orbit group

of points A_1 and A_2 by C_1

with respect to an axis of symmetry C_4

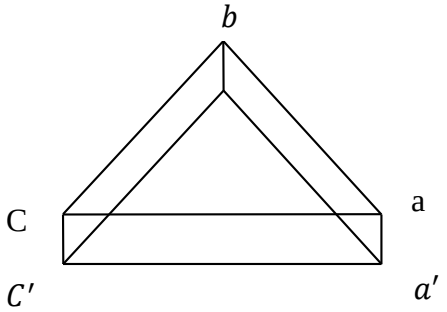
perpendicular to the face $A_1B_1C_1D_1$

for the following figure:

Exercise 10

- Determine the order of the double group

Dn of the following figure:



Exercise 11

Represent the different equivalent positions (equivalent images) of point P according to the symmetry operations 3_3, 3_1, and 3_2.

Exercise 12

Determine graphically the images A' of point A with respect to the slip planes represented by the symbols n, d, and a.

Exercise 13

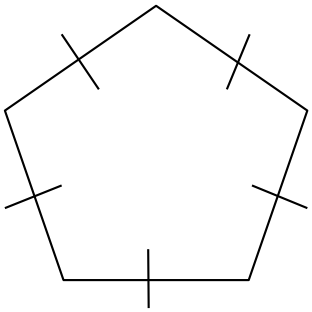
- Represent in 3D the point symmetry groups: 6/mmm, 4mm, 32, mmm, and 2/m.

- Provide the symmetry elements of each group and represent them in stereographic projection.

- Provide the multiplication tables for the point symmetry groups 2/m and 4mm.

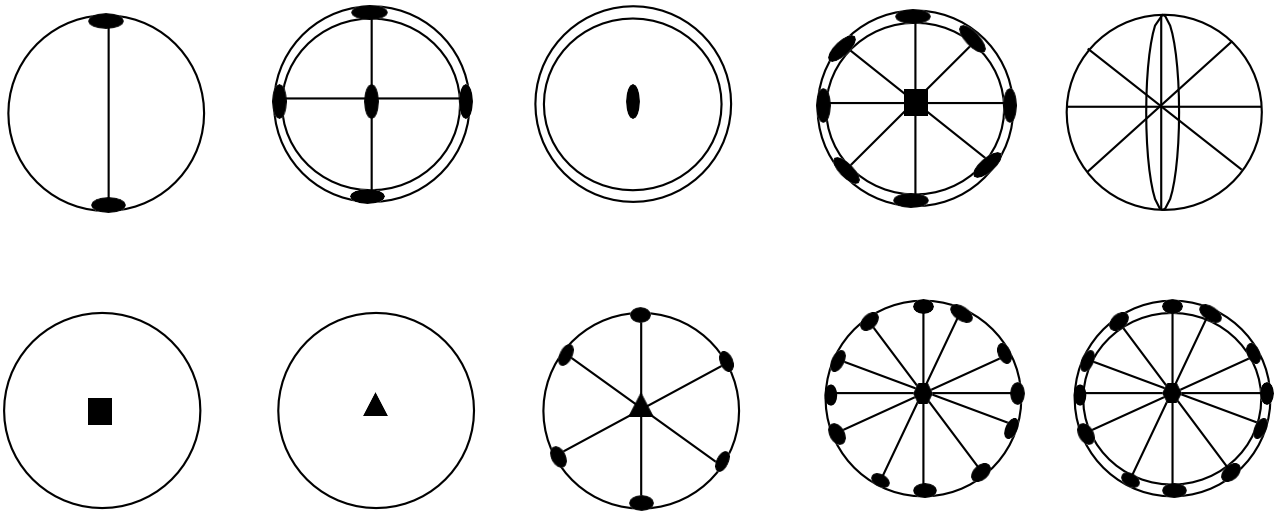
Exercise 14

Graphically show that the figure below does not possess an axis of order 5 in a crystal system.



Exercise 15

We provide the stereographic projections of the following symmetry elements:



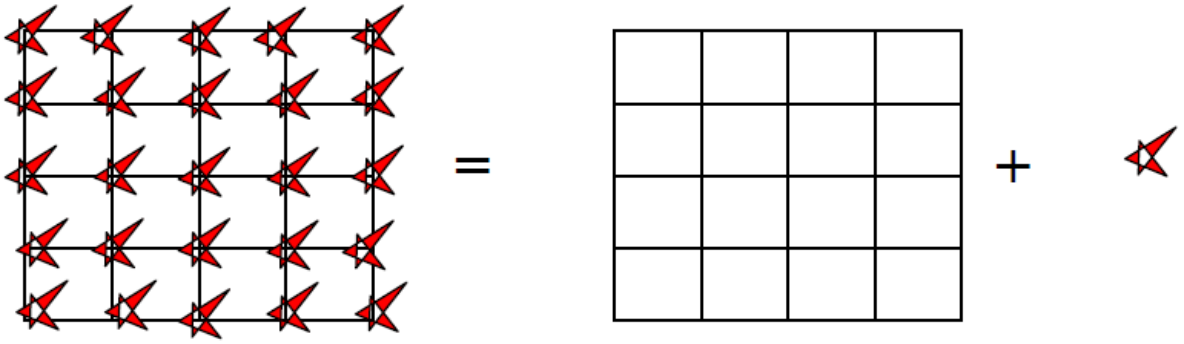
1- Determine the order of the symmetry axes and the position of the symmetry planes.

2- Give the point symmetry group of the projection.

CHAPTER II: Crystalline Structure

Introduction

The crystal is an infinite and regular stacking of identical patterns, a pattern that can be an atom, one or more molecules.



1.1 Crystal Lattice and System

1.1.1 Crystal lattice

a) Definition

A lattice is a regular periodic arrangement of points or nodes in space (the lattice is a pure mathematical concept).

To move from one node to another, it is sufficient to perform a translation $\vec{T}$ such that:

$$\vec{T} = n\vec{a} + m\vec{b} + p\vec{c}$$

In which n, m, p ∈ $\mathbb{Z}$ and $\vec{a}$, $\vec{b}$, $\vec{c}$ are the vectors of the crystal basis.

1.1.1.1 One-Dimensional Crystal Lattice (1D)

The translation vector on a one-dimensional (1D) lattice is: $\vec{T} = u\vec{a}$. Any direction that passes through two nodes is called a crystalline row $\vec{T} = u\vec{a}$ and is denoted by [u].

1.1.1.2 Two-Dimensional Crystal Lattice (2D)

The 2D crystal lattice is defined according to two basis vectors a ⃗ and b ⃗ such that the translation vector is the combination of the two:

$$\vec{T} = u\vec{a} + m\vec{b}$$

So, the vectors of the crystal basis are $\vec{a}$ and $\vec{b}$ with $\vec{a} = f(\overrightarrow{e_1}, \overrightarrow{e_2})$ and $\vec{b} = f(\overrightarrow{e_1}, \overrightarrow{e_2})$, therefore:

$$\begin{pmatrix} \vec{a} \\ \vec{b} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \overrightarrow{e_1} \\ \overrightarrow{e_2} \end{pmatrix}$$

A row of nodes is the direction [u,v]. Such that: $\vec{R} = u\vec{a} + v\vec{b}$.

1.1.1.3 Three-dimensional crystal lattice (3D)

The 3D crystal lattice is defined by three basis vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ and three angles that separate them: γ , β and α.

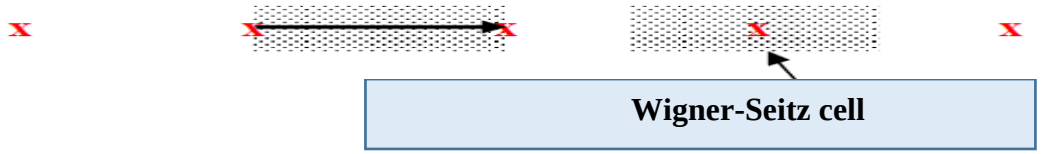
So, the vectors of the crystal basis are $\vec{a}$, $\vec{b}$ and $\vec{c}$ with $\vec{a} = f(\overrightarrow{e_1}, \overrightarrow{e_2}, \overrightarrow{e_3}), \vec{b} = g(\overrightarrow{e_1}, \overrightarrow{e_2}, \overrightarrow{e_3})$ and $\vec{c} = h(\overrightarrow{e_1}, \overrightarrow{e_2}, \overrightarrow{e_3})$, then:

$$\begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{22} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} \overrightarrow{e_1} \\ \overrightarrow{e_2} \\ \overrightarrow{e_3} \end{pmatrix}$$

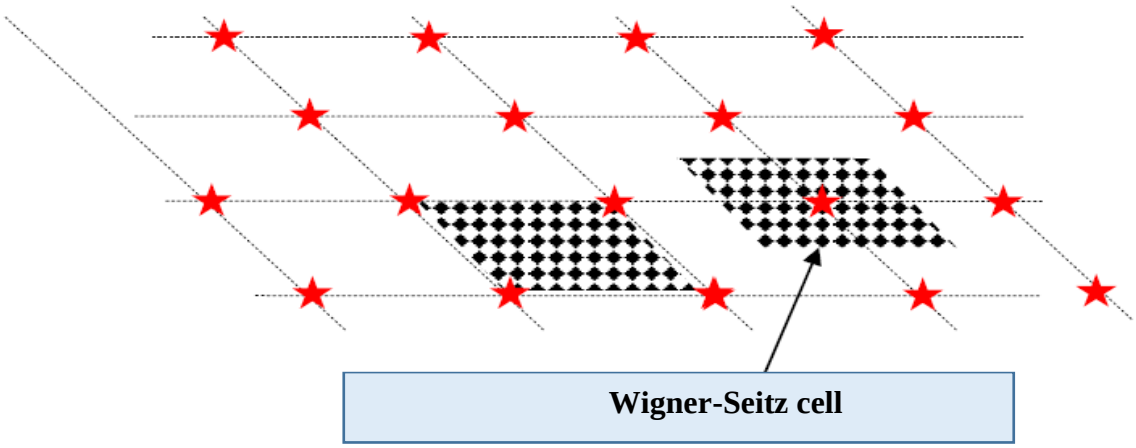
• A row of nodes is the direction [u,v,w]. Such that $\vec{R} = u\vec{a} + v\vec{b} + w\vec{c}$.

1.1.1.4 Primitive or Conventional Unit Cell

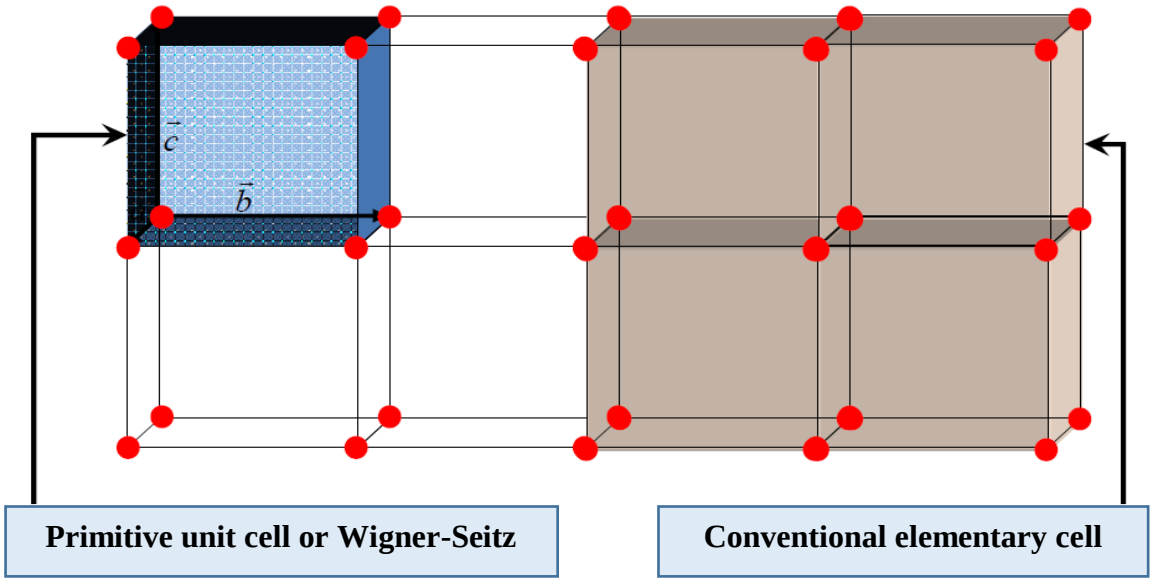
In 1D, any parallelogram constructed between two nodes or limited to a single node is called a primitive elementary cell.



In 2D, any parallelogram constructed between four nodes or limiting a single node is called a primitive unit cell or the smallest cell that has the point symmetry of the lattice and, by a simple translation, it gives the extent of the lattice.



In 3D, any parallelepiped constructed between eight nodes or limited to a single node is called a primitive unit cell or the smallest cell that has the point symmetry of the lattice and, through a simple translation, it gives the extent of the lattice.

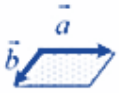
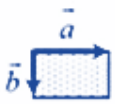
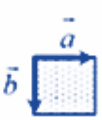


1.1.1.5 Conventional Elementary Cell

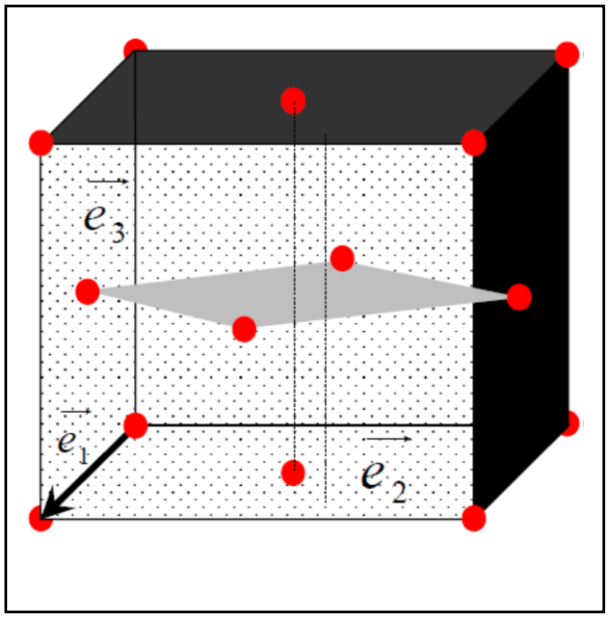
Any cell that contains more than one node is called a conventional elementary cell. Note:

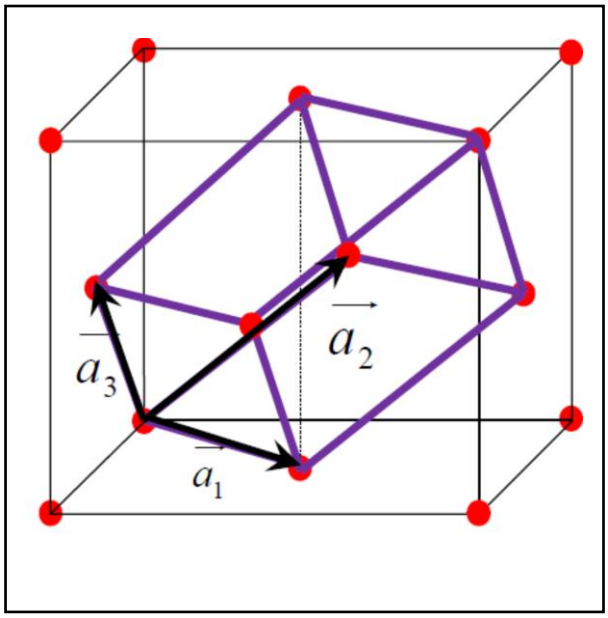
• The primitive unit cell contains a single node denoted P.

The following table represents all the 2D structures.

Crystal lattice	Parallelogram	Rectángulo	Square	Hexagon
Symmetry group	2	2mm	4mm	6mm
Primitive cell shape	$\begin{cases} \lvert\vec{a}\rvert \neq \lvert\vec{b}\rvert \\ \alpha \neq \pi/2 \end{cases}$ 	$\begin{cases} \lvert\vec{a}\rvert \neq \lvert\vec{b}\rvert \\ \alpha = \pi/2 \end{cases}$ 	$\begin{cases} \lvert\vec{a}\rvert = \lvert\vec{b}\rvert \\ \alpha = \pi/2 \end{cases}$ 	$\begin{cases} \lvert\vec{a}\rvert = \lvert\vec{b}\rvert \\ \alpha = \pi/3 \text{ ou } \alpha = 2\pi/3 \end{cases}$ 
Mode or type of network	p	p, c	p	p

Example: Face-centered cubic FCC or F.





$\vec{e}_1, \vec{e}_2, \vec{e}_3$ are the basis vectors associated with the conventional unit cell with a volume equal to $V = (a\vec{e}_1 \wedge a\vec{e}_2).a\vec{e}_3 = a^3$.

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the basis vectors related to the primitive unit cell and which contains a single node, with a volume that is equal to $V = (\vec{a}_1 \wedge \vec{a}_2).\vec{a}_3 = \left[\left(\frac{a}{2}\vec{e}_1 + \frac{a}{2}\vec{e}_2\right) \wedge \left(\frac{a}{2}\vec{e}_2 + \frac{a}{2}\vec{e}_3\right)\right]$.

$$\left(\frac{a}{2}\vec{e}_1 + \frac{a}{2}\vec{e}_3\right) = \frac{a^3}{8} + \frac{a^3}{8} = \frac{a^3}{4}$$

1.1.1.6 Fill Rate

The filling fraction is the actual occupancy rate of the space by the motifs that constitute a chosen unit cell.

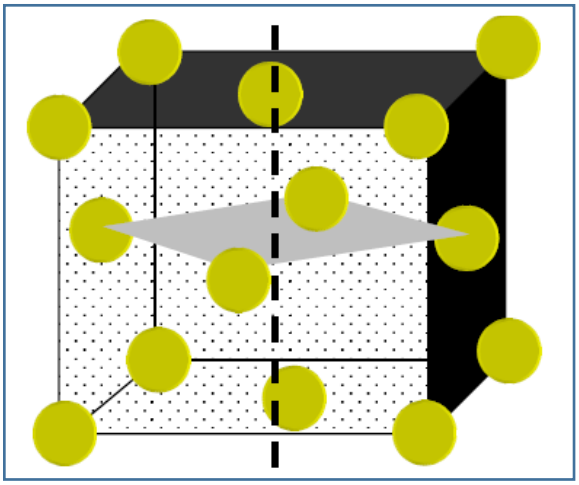
$$\tau = \frac{V\ Volume\ occupied\ by\ the\ atoms}{V\ Conventional\ unit\ cell\ volume}$$

Example: CFC Structure

$$\tau = \frac{\left(8 * \frac{1}{8} + 6 * \frac{1}{2}\right) 4\frac{\pi}{3} * r^3}{a^3}$$

Since $a\sqrt{2} = 4r \Rightarrow r = \frac{a\sqrt{2}}{4}$

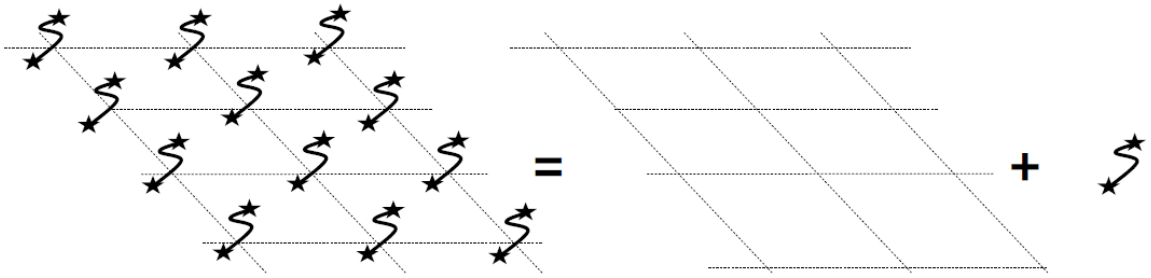
So, $\tau = \frac{4\frac{4}{3}\pi\frac{a^3 2\sqrt{2}}{4^3}}{a^3} = \frac{\pi\sqrt{2}}{6} = 74.05\%$



Application exercise: Calculate the packing density of a compact hexagonal structure.

1.1.2 Crystalline Basis

A physical crystal can be described by its lattice as well as a description of the arrangement of motifs (atoms, molecules, ions, dimers...) associated with this lattice. The motif or the crystalline basis must be identical in composition, orientation, and position.



The base may be composed of a single atom such as Cu, Ag, Al, or a molecule such as ZnS, CsCl, NaCl, or other ternary or quaternary compounds.

1.1.3 Bravais Lattice

In 1781, René Just Haüy (1743-1822) noticed by chance that certain rocks possess perfect shapes. In 1848, August Bravais showed that there can only be seven crystal systems. Also, he showed that the combination of these 7 crystal systems gives the following lattice modes:

$$3D\left\{\begin{array}{c} P: Primitive \\ I: Centred \\ F:\ Centred\ faces \\ S: Centred\ bases \\ A \\ B \\ C \end{array}\right\}, 2D\left\{\begin{matrix} P \\ C \end{matrix}\right\}, \{P\}$$

Generally, there are 14 Bravais lattices.

In our study, we are much more interested in the cubic or hexagonal structure simply because of the existence of this structure in the periodic table.

Application exercise

Determine in each Bravais lattice of cubic and hexagonal structure: Volume of the conventional cell, Number of nodes per cell, Volume of the primitive cell, Number of the 1st nearest neighbor, Distance between 1st nearest neighbors, Distance between 1st nearest neighbors, Distance between 2nd nearest neighbors, Filling coefficient τ

1.1.4 Reticular Plan and Inter-Reticular Distance

1.1.4.1 Definition

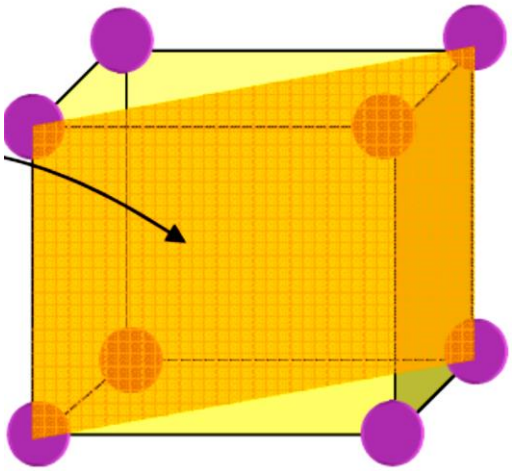
Another way to describe the crystal lattice is to assemble at least three parallel nodes or the equivalent of a plane called a "lattice plane."

1.1.4.2 Notation

The lattice plane is represented by the Miller indices h, k, and l as follows: (hkl). The distance between two consecutive planes of the same family is called the interplanar distance Dhkl.

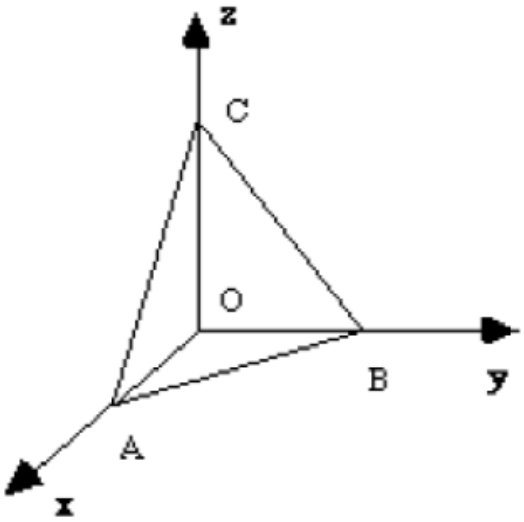
Example: The lattice plane (110).

The distance between the two planes of the same family {110} is: $d_{110} = \frac{\sqrt{2}}{2}$.



1.1.4.3 Representation of lattice planes (hkl)

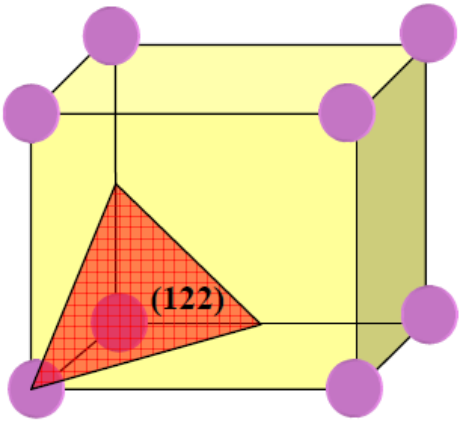
- In the first step, we find the coordinates of the intersections of the plane with the axes $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$. Let's imagine a plane that intersects the axes of any coordinate system at three nodes of the lattice A, B, C.



- The units chosen on the three axes are a, b, and c; we can write: OA = x.a, OB = y.b, and OC = z.c. The coordinates of A are (x,0,0); those of B are (0,y,0) and those of C are (0,0,z) where x, y, z are integers.
- Let's take their inverses 1/x, 1/y, 1/z and multiply them by their least common multiple. We obtain three numbers that are coprime to each other, h, k, l, which are the Miller indices of the considered plane. (Herman Joseph Miller, Prix Nobel 1946). The Miller indices of a plane are noted in parentheses: (h,k,l).

Example 1

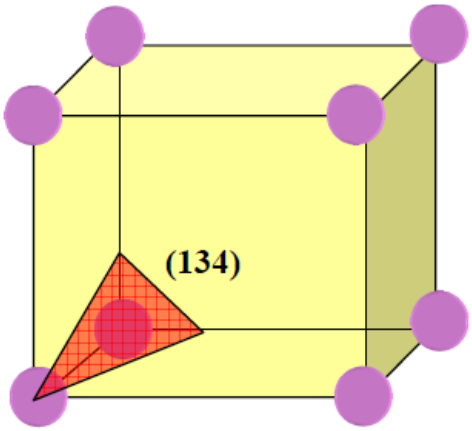
For the plane whose intersection coordinates are 1, 2, 2. For that, the inverses are 1, 1/2, 1/2. We multiply by the smallest integer multiplier. (2) So, the smallest integers being in the same ratio are 211, so the plan is (2/1, 1/2, 1/2), so it is (211).



Example 2

For the plane whose intersection coordinates are 1, 4, 3.

For that, the inverses are 1, 1/4, 1/3. We multiply by the smallest integer multiple. (12) So, the smallest integers in the same ratio are 12, 4, 3, so the plan is (12/12, 3/12, 4/12), which is (1, 1/4, 1/3).



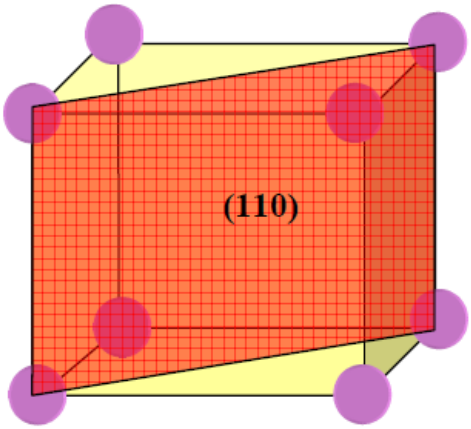
Particular cases

If one of the intersections is rejected to infinity, then the corresponding index is zero. Example (102) represents the intersection 1, ∝, ½.

If a plane intersects the negative part of an axis, the corresponding index is negative, so the minus sign is placed above the index as in $(1\bar{1}0)$.

Example 3:

For the plane whose intersection coordinates are 1, 1, 0. For that, the inverses $\frac{1}{1}, \frac{1}{1}, \frac{1}{0}$. We multiply by the smallest integer multiplier. (1) So, the smallest integers in the same ratio are 1 1 ∝, so the plane is (1, 1, ∝), therefore it is (11∝)

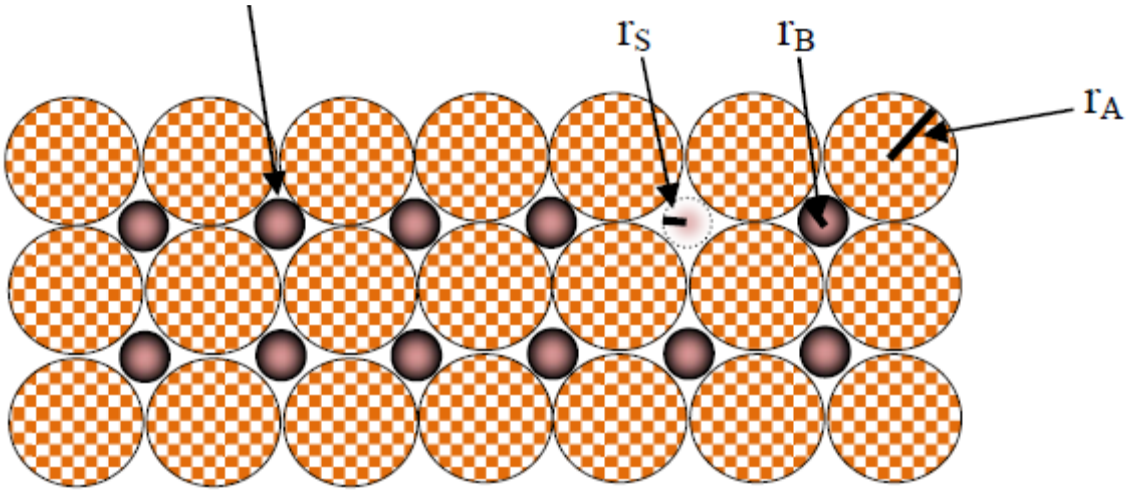


1.2 Models of Crystal Structure

There are five models of the most well-known crystalline structures in nature, which are:

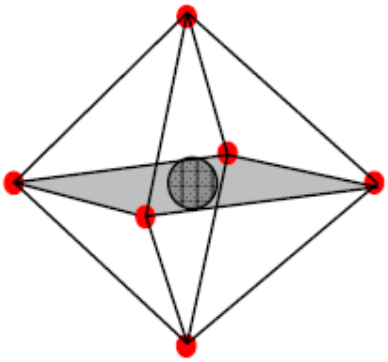
1. NaCl Model
2. CsCl Model
3. Diamond Model
4. ZnS Model
5. Fluorine model CaF_2

The classification of the models depends on the nature of the bond between the motifs. For example, Na-Cl or Cs-Cl, C-C, Zn-S or F-Ca. So, it is related to stable or unstable positions.



So the stability condition is $r_B < rS$, where r_B and r_S are the atomic radii of element B and site S, respectively.

The sites that can be occupied by foreign atoms must satisfy the stability condition rB < rS for the structure to be stable. In general, only the three types of interstitial sites exist.

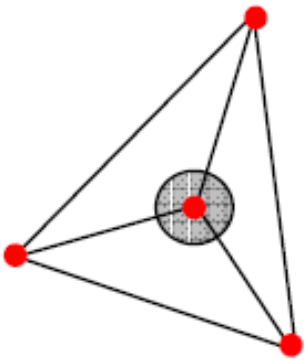


a. Octahedral site

It is located at the center of a cavity formed by 6 spheres.

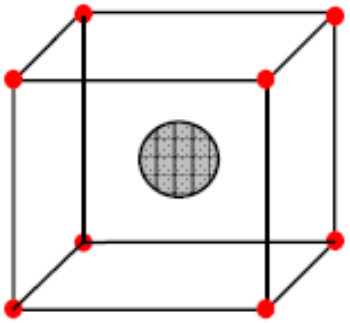
b. Tetrahedral site

It is located at the center of a cavity formed by 4 spheres.



c. Site C

It is located at the center of a cavity formed by 8 spheres.

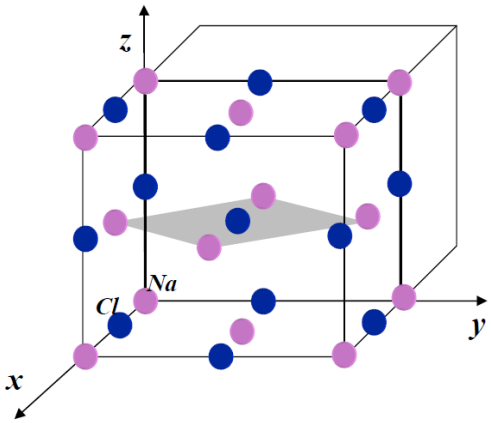


1.2.1 NaCl Model (Na+Cl-):

a. The structure of sodium chloride NaCl crystallizes in a face-centered cubic lattice, and the crystal basis consists of one Na atom and one Cl atom separated by half a diagonal of the cube, thus: Na: 000; ½½0; ½0½; 0½½, Cl: ½½½; 00½; 0½0; ½00

Each Cl atom is surrounded by six Na atoms.

- The Na+ ions occupy the nodes of the FCC lattice.
- The Cl- ions occupy the octahedral sites of the FCC lattice.



b. Stability condition

$$a = 2r_{Na} + 2r_S, \text{ thus } r_S = \frac{a}{2} - r_{Na}$$

Therefore $$r_B < r_S \Rightarrow r_{Cl} < \frac{a}{2} - r_{Na}$$

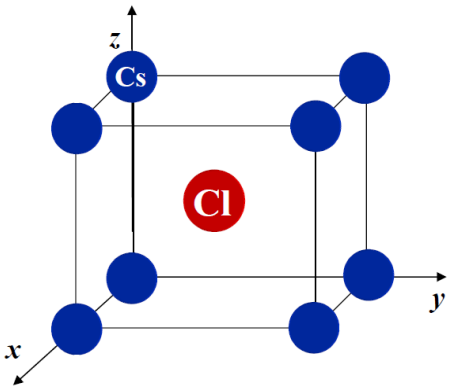
We notice that the Bravais lattice of NaCl is CFC and that the CFC of Na is offset from the CFC of Cl by a/2. Materials possess the structure LiF, MgO, MnO, AgBr….

1.2.2 CsCl Model (Cs+Cl-):

The structure of cesium chloride CsCl crystallizes in a simple cubic lattice and the crystal base consists of one Cs atom and one Cl atom separated by half a diagonal of the cube, thus:

Cs: 000

Cl: ½½½



Each Cl atom is surrounded by eight Cs atoms.

- The Cs+ ions occupy the nodes of the simple cubic lattice. The Cs+ ions occupy the nodes of the simple cubic lattice.The Cl- ions occupy the sites C.

Stability condition

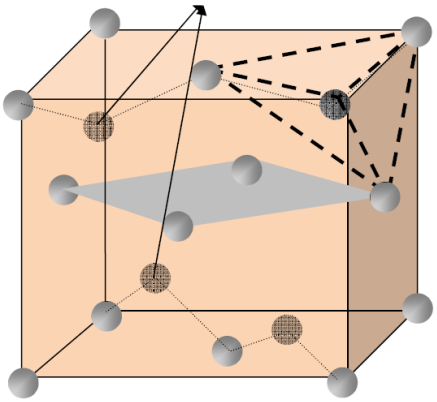
The site C, $\sqrt{3}a = 2r_{Cs} + 2r_S$, $r_s = \frac{\sqrt{3}a}{2} - r_{Cs}$

So, $r_B < r_S \Rightarrow r_{Cl} < \frac{\sqrt{3}a}{2} - r_{Cs}$,

It is noted that the Bravais lattice of CsCl is simple cubic and that the simple cubic of Cs is offset from the simple cubic of Cl by $\frac{\sqrt{3}a}{4}$. Materials that possess the CsCl structure: AlNi, CuZn, CuPd.

1.2.3 Diamond Model

The diamond lattice is FCC, whose crystal base contains two carbon atoms C with (0,0,0) and (¼ ¼ ¼). The conventional unit cell contains 8 carbon atoms, of which 4 atoms form the FCC and 4 atoms are placed in the tetrahedral sites with the coordinates: (1/4, 1/4, 1/4), (3/4, 3/4, 1/4), (3/4, 1/4, 3/4).



Conventional diamond lattice

The tetrahedral sites are half-filled, that is, 4 sites out of the 8 vacant sites. The bond is covalent.

Example: Silicium, Carbone, Germanium.

Note:

Diamond is composed of two FCC lattices, one offset relative to the other by $\frac{\sqrt{3}a}{4}$.

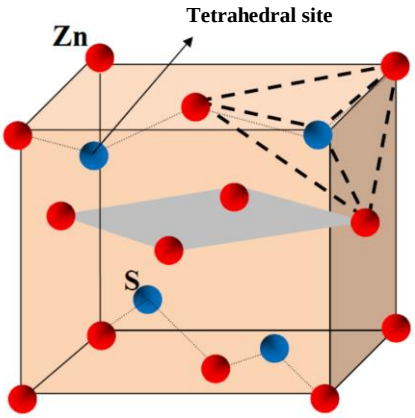
1.2.4 ZnS **Model**

The ZnS lattice is the same as that of diamond except that the crystal base changes. Instead of carbon atoms placed in tetrahedral sites, sulfur atoms S are placed. The conventional unit cell contains 4 carbon atoms and 4 sulfur atoms, with the Zn atoms occupying the FCC nodes and the sulfur atoms occupying 50% of the tetrahedral sites according to the following

coordinates:

Zn: (000)

S : (¼ ¼ ¼), (¾ ¾ ¼), (¾ ¼ ¾), (¼ ¾ ¾).



Conventional lattice of ZnS

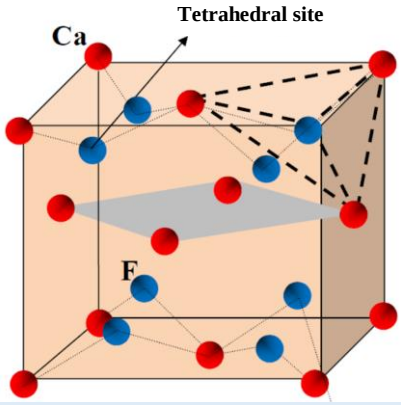
The tetrahedral sites are half-filled, that is, 4 sites out of 8. The bond in ZnS is a covalent bond. Stability condition:

The site T, $\frac{\sqrt{3}a}{2} = 2r_{Zn} + 2r_{Site}$, $r_{site} = \frac{\sqrt{3}a}{4} - r_{Zn}$

So, $r_s < r_{Site} \Rightarrow r_S < \frac{\sqrt{3}a}{4} - r_{Zn}$.

The ZnS lattice is face-centered cubic, and the face-centered cubic lattice of Zn is offset from the CFC of S by $\frac{\sqrt{3}a}{4}$.

1.2.5 Fluorine Model CaF_2



Conventional lattice of CaF_2

The structure of fluorite (CaF_2) is the same as that of diamond or ZnS, with the only difference being that the fluorine atoms occupy the 8 tetrahedral sites. The conventional unit cell contains 4 Ca atoms and 8 fluorine atoms, with the Ca atoms occupying the FCC nodes and the fluorine atoms occupying 100% of the tetrahedral sites according to

The following coordinates:

Ca: (000)

F: (¼ ¼ ¼), (¾ ¼ ¼), (¼ ¾ ¼), (¾ ¾ ¼), (¼ ¼ ¾), (¾ ¼ ¾), (¼ ¾ ¾), (¾ ¾ ¾).

The tetrahedral sites are completely filled, meaning that all 8 tetrahedral sites are occupied. The bond in CaF_2 is a covalent bond.

Serie 2: Crystalline Structure

Serie N^0 02 : Crystalline Structure

Exercise 01

We consider two orthorhombic lattices I and F with crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$. Show that the vectors $\overrightarrow{a'}$, $\vec{b}'$, $\overrightarrow{c'}$ described below are primitive vectors for the following cases.

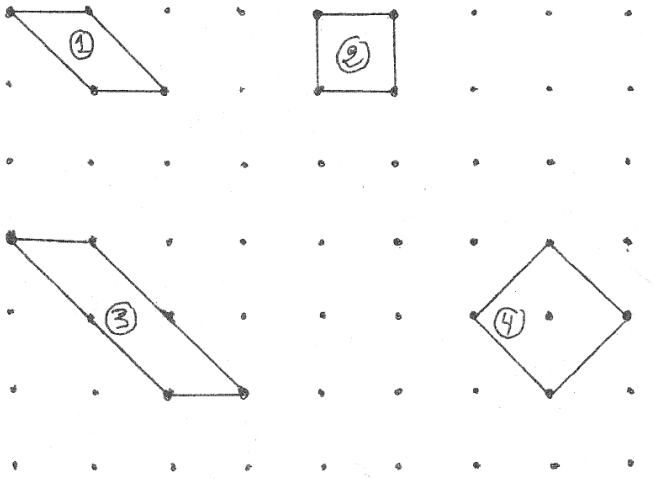
Orthorhombic I lattice: $\overrightarrow{a'} = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$; $\overrightarrow{b'} = \frac{1}{2}(\vec{b} + \vec{c} - \vec{a})$; $\overrightarrow{c'} = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c})$.

Orthorhombic F lattice: $\overrightarrow{a'} = \frac{1}{2}(\vec{b} + \vec{c})$; $\overrightarrow{b'} = \frac{1}{2}(\vec{c} + \vec{a})$; $\overrightarrow{c'} = \frac{1}{2}(\vec{a} + \vec{b})$.

Exercise 02

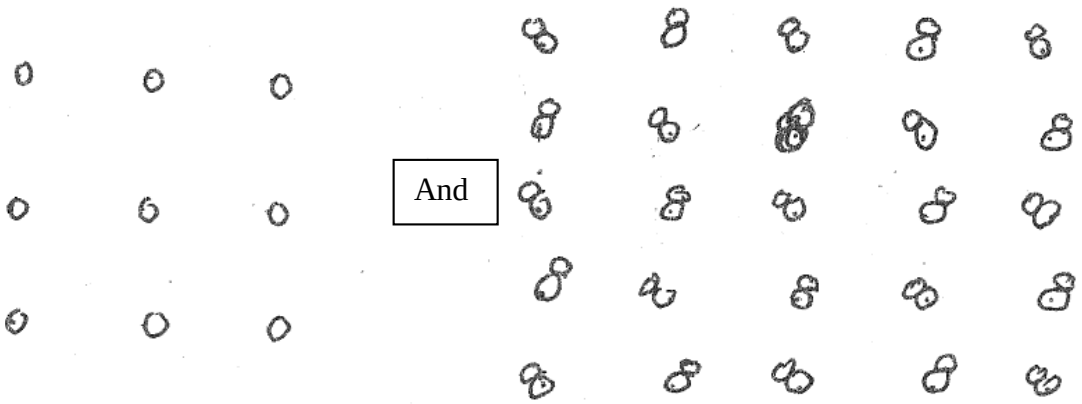
We consider the following two-dimensional network:

1) How many nodes do the represented meshes contain?
2) What is the multiplicity of these meshes?
3) What is the area of these cells (given by the dot product of the vectors that define them)?
4) What are the symmetry elements of the lattice?



Exercise 03

We consider two planar crystals composed of identical atoms symbolized by circles.



1) Determine the lattice of each of these crystals. Represent the unit cell.
2) Represent the motif, how many atoms does it have.

Exercise 04

Show that only rotation axes of order 2, 3, 4, and 6 are compatible with the triple periodicity of the lattice.

Exercise 05

Oxygen crystallizes in the cubic system with a parameter a = 683 pm. The density of the solid is 1.32 Kg/m³. How many molecules of dioxygen does the unit cell contain?

Determine the number of nearest neighbors as well as their distance from the FCC lattice (we will stop at the 5th nearest neighbors).

Exercise 06

We consider a body-centered cubic system.

1) Plot the crystal planes (100), (110), and (111).

2) Determine the lattice density of each of these planes.

3) Determine the node density per unit volume.

4) Deduce the expression of the lattice planes in the families (100), (110), and (111).

Exercise 07

Determine the indices [mnp] of the row that passes through the two nodes of the network m1, n1, p1 and m2, n2, p2.

Exercise 08

Determine the interplanar distance d_{hkl} between the crystal planes in the following cases:

a) Simple cubic, b) Body-centered cubic, c) Face-centered cubic, d) Hexagonal.

Exercise 09

By treating the atoms of an element as hard spheres of radius r, calculate the packing fraction achieved when this element crystallizes in a structure:

a) Simple cubic b) Body-centered cubi c) Face-centered cubic d) Diamond e) Hexagonal close-packed (we will calculate the c/a ratio)

Exercise 10

Using a reciprocal lattice property, establish the condition that allows a row [mnp] to be contained in a plane (hkl).

Application: Is the row $[\bar{2}10]$ contained in the plane (123)?

Exercise 11

Determine the reciprocal network of the following systems:

a) CS, b) CC, c) CFC, d) hexagonal.

Exercise 12

a) Show that any vector of the reciprocal lattice ($\vec{G}_{hkl}$) is perpendicular to the planes with the same indices (hkl) in the direct space.

b) Show that the distance d_{hkl} between two consecutive (hkl) planes is inversely proportional to $|(\vec{G}_{hkl})|$.

c) Deduce the expression for d_{hkl}:

- For a CS network
- For an orthorhombic

Exercise 13

We successively consider the direct lattices: SC, FCC, BCC (all with lattice parameter a). In the reciprocal space, evaluate the volume of the corresponding elementary cells.

Exercise 14

We consider an orthorhombic lattice I.

1) Show that the RR of the O.I network is an O.F network whose crystal parameters will be given. From this, deduce the reciprocal vector as well as the lattice distance.

2) We consider a CS network: Determine its RR as well as d_{hkl}.

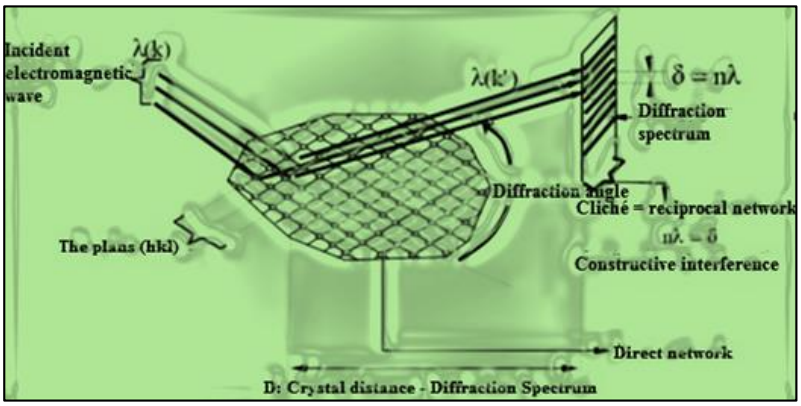
Determine the wavelength of an X-ray beam striking the crystal along a family of lattice planes (123) at an angle $\theta = 45°$ and undergoing first-order reflection.

Chapter III Analysis of X-ray Diffractions

2.1 Principle

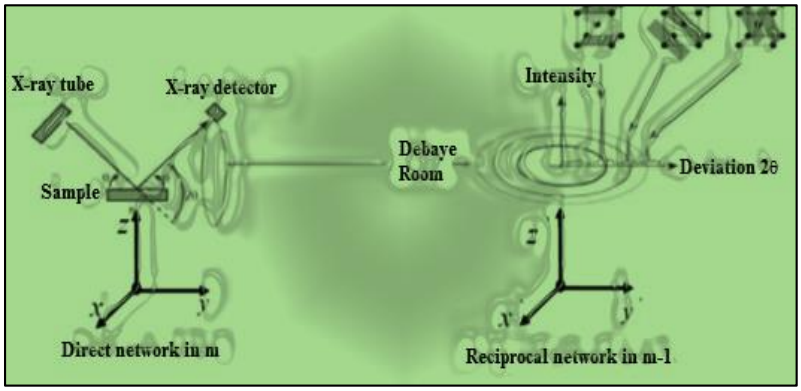
Crystals can be considered as assemblies of lattice planes. The planes are formed by atoms, molecules, or other patterns. These lattice planes are separated by characteristic distances d_{hkl} according to the nature of the crystal.

With radiation (electromagnetic wave) of sufficiently small wavelength, we obtain the phenomenon of diffraction by the crystal lattice planes.



2.2 Reciprocal lattice (photograph)

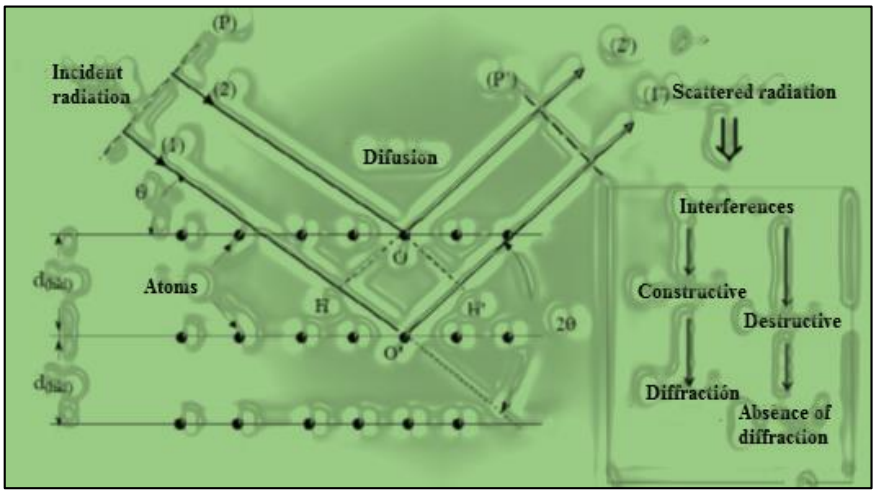
To describe diffraction, the concept of the reciprocal lattice is introduced, which represents the interferences on the diffraction pattern.



We observe the phenomenon of diffraction in a given direction if the interaction between the X-rays and the lattice planes gives rise to constructive interference. These are ensured by the Bragg condition.

2.3 Bragg Condition (1890-1971)

Let there be two waves arriving on two lattice planes at an incident angle θ and scattered at the same angle, the path difference between the two waves on planes P and P' is:



We have the step difference δ is:

$\delta = HO + O'H' = 2d_{hkl} \sin\theta_{(hkl)}$

Diffraction will occur when the condition for constructive interference is met, namely:

$$\delta = n\boldsymbol{\lambda}$$

The diffraction condition, known as Bragg's condition, is then:

$$2d_{(hkl)} sin\theta_{(hkl)} = n_{(hkl)}\lambda$$

This equation represents the fundamental relationship that governs diffraction.

2.4 Transition from the direct lattice to the reciprocal lattice

The set of all wave vectors $\vec{k}$ that produce a plane wave with a periodicity equal to that of a Bravais lattice is called the reciprocal lattice.

$$\text{So } e^{i\vec{k}(\vec{r}+\vec{R})} = e^{i\vec{k}(\vec{r})} \Rightarrow e^{i\vec{k}(\vec{r})}.e^{i\vec{k}(\vec{R})} = e^{i\vec{k}(\vec{r})}$$

$$e^{i\vec{k}(\vec{R})} = 1 =. e^{0} \Rightarrow \vec{k}.\vec{R} = 2\pi$$

From the last relation, we notice that the dimension of k is m^{-1}.

It is assumed that the vectors $\overrightarrow{a_1}, \overrightarrow{a_2}$ and $\overrightarrow{a_3}$are the fundamental basis vectors of the direct lattice and $\overrightarrow{a_1^*}, \overrightarrow{a_2^*}$ and $\overrightarrow{a_3^*}$are those of the reciprocal lattice, so we need to find the link between:

$$\begin{Bmatrix} \overrightarrow{a_1^*} \perp (\overrightarrow{a_2}, \overrightarrow{a_3}) \\ \overrightarrow{a_2^*} \perp (\overrightarrow{a_1}, \overrightarrow{a_3}) \\ \overrightarrow{a_3^*} \perp (\overrightarrow{a_1}, \overrightarrow{a_2}) \end{Bmatrix}, \text{ so } \begin{Bmatrix} \overrightarrow{a_1^*}.\overrightarrow{a_1} = 2\pi \\ \overrightarrow{a_1^*}.\overrightarrow{a_2} = 0 \\ \overrightarrow{a_1^*}.\overrightarrow{a_3} = 0 \end{Bmatrix}, \text{ so } \overrightarrow{a_i^*}.\overrightarrow{a_j} = 2\delta_{ij},$$

Such that δ_{ij} d is the Kronecker symbol with $\begin{Bmatrix} 1\ si\ i = j \\ 0\ si\ i \neq j \end{Bmatrix}$

So, we can write the general relationship:

$$\begin{Bmatrix} \overrightarrow{a_1^*} = \frac{2\pi}{V}(\overrightarrow{a_2} \wedge \overrightarrow{a_3} \\ \overrightarrow{a_2^*} = \frac{2\pi}{V}(\overrightarrow{a_1} \wedge \overrightarrow{a_3} \\ \overrightarrow{a_3^*} = \frac{2\pi}{V}(\overrightarrow{a_1} \wedge \overrightarrow{a_2} \end{Bmatrix} V \text{ is the direct network volume.}$$

So, in matrix form, we write it as:

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{22} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} . \begin{bmatrix} \overrightarrow{a_1^*} \\ \overrightarrow{a_2^*} \\ \overrightarrow{a_3^*} \end{bmatrix} = \begin{bmatrix} \overrightarrow{a_1} \\ \overrightarrow{a_2} \\ \overrightarrow{a_3} \end{bmatrix}$$

If we multiply everything by $\overrightarrow{a_1}$, we find:

$$\overrightarrow{a_1}.\overrightarrow{a_1} = (\alpha_{11}.\overrightarrow{a_1^*} + \alpha_{12}.\overrightarrow{a_2^*} + \alpha_{13}.\overrightarrow{a_3^*}).\overrightarrow{a_1} \Leftrightarrow a_1^2 = \alpha_{11}.2\pi$$

So, we can determine the components of the matrix as follows:

$$\alpha_{11} = \frac{a_1^2}{2\pi}, \alpha_{22} = \frac{a_2^2}{2\pi}, \alpha_{33} = \frac{a_3^2}{2\pi}.$$

For the other components

$$\overrightarrow{a_1}.\overrightarrow{a_2} = (\alpha_{11}.\overrightarrow{a_1^*} + \alpha_{12}.\overrightarrow{a_2^*} + \alpha_{13}.\overrightarrow{a_3^*}).\overrightarrow{a_2} \Leftrightarrow a_1.a_2\cos(\gamma) = \alpha_{12}.2\pi$$

$$\text{So } \alpha_{12} = \frac{a_1.a_2\cos(\gamma)}{2\pi}$$

So for all the components of the matrix, we have:

$$\begin{bmatrix} a_1^2 & a_1.a_2\cos(\gamma) & a_1.a_3\cos(\beta) \\ a_2.a_1\cos(\gamma) & a_2^2 & a_2.a_3\cos(\alpha) \\ a_3.a_1\cos(\beta) & a_3.a_2\cos(\alpha) & a_3^2 \end{bmatrix} . \begin{bmatrix} \overrightarrow{a_1^*} \\ \overrightarrow{a_2^*} \\ \overrightarrow{a_3^*} \end{bmatrix} = \begin{bmatrix} \overrightarrow{a_1} \\ \overrightarrow{a_2} \\ \overrightarrow{a_3} \end{bmatrix}$$

2.5 Diffraction Conditions (Laue Condition)

The main characteristic of the crystal being its periodicity. This is verified for all physical quantities associated with the crystal. Let a physical quantity be defined by f(r), thus:

$\forall \vec{r},\ \forall \vec{R}; f\left(\vec{r}+\vec{R}\right)=f(\vec{r})$ where $\vec{r}$ is the position vector and $\overrightarrow{R}$ is the translation vector. Using the Fourier series:

$$f(\vec{r})=\sum A_k e^{i(\vec{k}.\vec{r})} \Leftrightarrow f(\vec{r})=\sum A_k e^{i\overrightarrow{k}.(\vec{r}+\vec{R})}$$

Such as $$A_k=\frac{1}{V}\int f(\vec{r})e^{i(\vec{k}.\vec{r})}\overrightarrow{dr}$$

So $$f\left(\vec{r}+\vec{R}\right)=f(\vec{r}) \Leftrightarrow e^{i(\vec{k}.\vec{R})}=1 \Leftrightarrow \overrightarrow{k}.\vec{R}=2\pi$$

By expressing the vector $\vec{k}$ as a linear combination of integer coefficients such as:

$$\vec{k}=h\overrightarrow{a_1^*}+k\overrightarrow{a_2^*}+l\overrightarrow{a_3^*} \rightarrow (hkl)$$

2.6 Miller Indices and Lattice Distance in the Reciprocal Lattice

The most important property of the reciprocal lattice RL is that each row of the reciprocal lattice passing through the origin represents a family of lattice planes of the direct lattice.

So $\overrightarrow{G_{hkl}}\perp$(hkl)

We know that $$\overrightarrow{G_{hkl}}=h\overrightarrow{a_1^*}+k\overrightarrow{a_2^*}+l\overrightarrow{a_3^*}$$

We use the relation LD → RL which gives that:

$$\overrightarrow{a_i^*}.\overrightarrow{a_j}=2\delta_{ij} \text{avec} \begin{cases} 1\ si\ i=j \\ 0\ si\ i\neq j \end{cases}$$

So, we find $$d_{hkl}=\frac{2\pi}{|\overrightarrow{G_{hkl}}|}$$

Application: Simple cubic lattice SC

We know that the basis vectors of the CS are:

$$\overrightarrow{G_{hkl}} = h(\frac{2\pi}{a}\overrightarrow{e_1}) + k(\frac{2\pi}{a}\overrightarrow{e_2}) + l(\frac{2\pi}{a}\overrightarrow{e_3})$$

So, $$|G_{hkl}| = \frac{2\pi}{a}\sqrt{h^2 + k^2 + l^2}$$

So the lattice distance is:

$$d_{hkl} = \frac{2\pi}{|\overrightarrow{G_{hkl}}|} = \frac{2\pi}{(\frac{2\pi}{a})\sqrt{h^2 + k^2 + l^2}}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Application:

For the family (100), the distance is $d_{100} = a$

For the family (111), the distance is $d_{111} = \frac{a}{\sqrt{3}}$

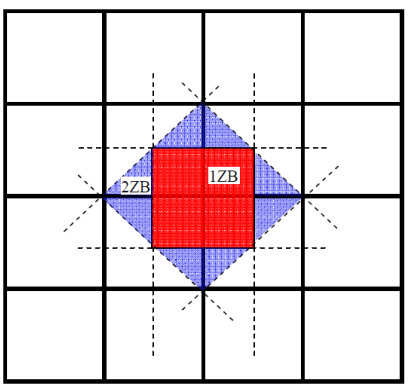
Similarly, we find the expressions for the lattice distance as a function of the Miller indices.

2.7 Brillouin Zone (RL)

As in the direct lattice, where a primitive cell called the Wigner-Seitz cell is constructed, a primitive cell can also be represented in the reciprocal lattice RL, which is called the Brillouin zone. It is also possible to define several Brillouin zones, which are named:

- 1st Brillouin zone (1BZ)
- 2nd Brillouin zone (2BZ)
- 3rd Brillouin zone (3BZ)

Application: Construction of the 1st, 2nd, and 3rd Brillouin zones for a square system.



Note:

1- It can be shown that the volume of the 1st Brillouin zone is equal to the volume of all other Brillouin zones, 2nd, 3rd, ... nth.

So,

Punto	k en 2π/a	Commentary
Γ	(0,0,0)	Center of the 1BZ
X	(0,1,0)	In the direction (010)
L	(½,½,½)	In the direction (111)
K	(¾,¾,0)	In the direction (330)
W	(½,1,0)	In the direction (120)

V1BZ = V2BZ = V3BZ …… = VnBZ

2- In the reciprocal network, we always talk about special points such as

Special directions:

- **Δ (Γ → Ξ)**
- **∧ ((Γ → Λ)**
- **$Z(X \rightarrow W)$**
- **$\Sigma(\mu \rightarrow W)$**

2.8 Identification of crystalline structures:

IV.4.8.1 Intensity of the electromagnetic wave diffracted by a crystal:

The diffracted intensity I at a point in space is proportional to the square of the wave function vector, therefore:

$$I(\overrightarrow{k'}) \propto \Psi^2_{(x,y)} = AA^*$$

With A being the amplitude of the diffracted wave, the intensity is given by:

$$I(\vec{k}) = \frac{C^2 E_0^2}{d^2} FF^* \frac{Sin^2\left[\frac{N}{2}(\Delta\vec{k}.\vec{a}_1\right]}{Sin^2\left[\frac{1}{2}(\Delta\vec{k}.\vec{a}_1\right]}. \frac{Sin^2\left[\frac{N}{2}(\Delta\vec{k}.\vec{a}_2\right]}{Sin^2\left[\frac{1}{2}(\Delta\vec{k}.\vec{a}_2\right]}. \frac{Sin^2\left[\frac{N}{2}(\Delta\vec{k}.\vec{a}_3\right]}{Sin^2\left[\frac{1}{2}(\Delta\vec{k}.\vec{a}_3\right]}$$

Such that:

d: the distance between the film (negative) and the crystal lattice.

$\Delta\vec{k} = \overrightarrow{k'} - \vec{k}$: Variation of the wave vector.

F: Structure factor.

C: constant.

So, for the structure factor, we write it as follows:

$$F = \sum_{i=0}^{s} f_i . e^{j(\Delta\vec{k}.\overrightarrow{R_l})}$$

With i: the number of atoms in the crystal lattice and R: position vector of the atom. Experimentally, when F = Fmax → in the image, we find bright regions.

and when F = Fmin → in the image, we find dark regions.

So, the term that will influence the intensity is the structure factor, which can be written as follows:

$$F = \sum_{i=0}^{s} f_i . e^{-j2\pi(h\vec{u}+k\vec{v}+l\vec{m})}$$

2.8.1 Application

a / Structure cubic (CS):

In the case of a simple cubic structure, the multiplicity (Z= 1) is represented by (0,0,0), therefore, the structure factor is written as follows:

$$F = \sum_{i=0}^{s} f_i . e^{-j2\pi(h\vec{0}+k\vec{0}+l\vec{0})}$$

$$F = \sum_{i=0}^{s} f_0$$

So, whatever the h, k, and l, the F factor is maximal. So all the lattice planes (hkl) reflect the light.

Extinction condition du CS $\Rightarrow \forall\, h,k,l \;\rightarrow I = \gamma f_0^2$

So, the planes that will be represented in diffraction are:

$n=h^2+k^2+l^2$	Possible plans	Plans (hkl) for CS
01	100	100
02	110	110
03	111	111
04	200	200
05	210	210
06	211	211
07		
08	220	220
09	300 ou 221	300 ou 221

b / Cubic structure (CC):

In the case of a body-centered cubic structure, the motif is represented by the reduced coordinates (0,0,0) and (½, ½,½), therefore, the structure factor is written as follows:

$$F = \sum_{i=0}^{s}(f_i.e^{-j2\pi(h\vec{0}+k\vec{0}+l\vec{0})} + e^{-j\pi(h+k+l)}) = f_i.(1 + cos\pi(h+k+l))$$

So, for F to be maximal, it is necessary that cos □ (h + k + l) = 1, which means that h + k + l must be even. So, the extinction conditions are:

$$\begin{cases} \forall\ h,k,l \\ \text{et} \\ h+k+l = 2n \end{cases} \Rightarrow \boxed{h+k+l=2n}$$

So, the planes that will be represented in diffraction are:

Extinction condition du CC $\Rightarrow h+k+l=2n \rightarrow I = 4\gamma f_0^2$

So, for F to be maximal, it is necessary that $cos\ \theta(h+k+l) = 1$, so it is necessary that

$n=h^2+k^2+l^2$	Possible plans	Plans (hkl) for CC
01	100	
02	110	110
03	111	
04	200	200
05	210	
06	211	211
07		
08	220	220
09	300 ou 221	
10	310	310
11	311	
12	222	222
13	320	
14	321	321

c/ Cubic structure (FCC):

In the case of a face-centered cubic structure, the multiplicity (Z=2) is represented by the reduced coordinates (0,0,0), (½, ½,0), (0, ½, ½), and (½,0, ½).

therefore, we write the structure factor as follows:

$$F = \sum_{i=0}^{s}(f_i . e^{-j2\pi(h\vec{0}+k\vec{0}+l\vec{0})} + e^{-j2\pi(\frac{h}{2}+\frac{k}{2})} + e^{-j2\pi(\frac{k}{2}+\frac{l}{2})} + e^{-j2\pi(\frac{h}{2}+\frac{l}{2})})$$

$$F = \sum_{i=0}^{s} . f_i(1 + cos\pi(h+k) + cos\pi(k+l) + cos\pi(h+l)$$

So, for F to be maximal, the three terms must have the same parity.

$$\begin{Bmatrix} cos\pi(h+k) = 1 \\ cos\pi(k+l) = 1 \\ cos\pi(h+l) = 1 \end{Bmatrix}$$

So, the conditions for extinction are:

$$\begin{Bmatrix} (h,k,l) = 2n \\ ou \\ (h,k,l) = 2n+1 \end{Bmatrix}$$

Extinction condition du CFC $\Rightarrow h, k, l: 2n$ ou $h, k, l: 2n+1 \rightarrow I = 16\gamma f_0^2$

So, the planes that will be represented in diffraction are:

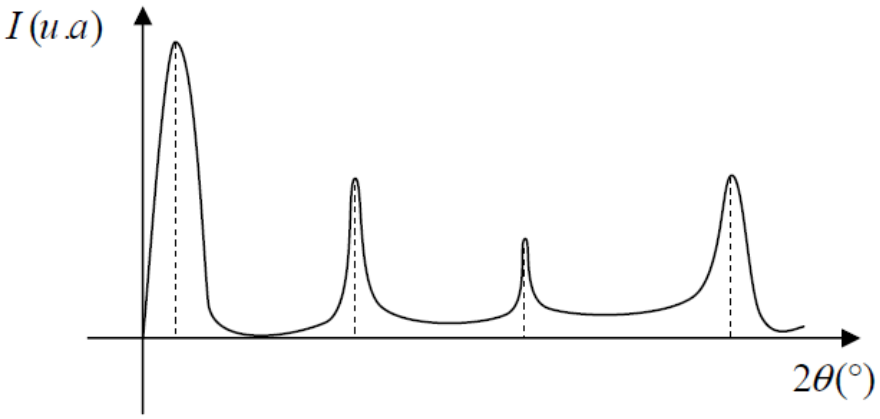
$n=h^2+k^2+l^2$	Possible plans	Plans (hkl) for CFC
01	100	
02	110	
03	111	111
04	200	200
05	210	
06	211	
07		
08	220	220
09	300 ou 221	
10	310	
11	311	311
12	222	222
13	320	
14	321	
15		
16	400	400
17	410 ou 322	

In the following table, the extinction conditions for different crystal structures are given:

Crystalline structural	Extionction condition on the (hkl)	Structural factor	Intensity $I = \gamma_{max} F.F^*$
CS	$\forall h, k, l$	f_0	$\gamma_{max} f_0^2$
CC	$h+k+l=2n$	$2f_0$	$4\gamma_{max} f_0^2$
CFC	$h,k,l:2n$ $h,k,l:2n+1$	$4f_0$	$16\gamma_{max} f_0^2$
Diamond	$h+k+l=2n+1$	$4f_0$	$16\gamma_{max} f_0^2$
	$h+k+l=2(2n+1)$	$8f_0$	$64\gamma_{max} f_0^2$
Hexagonal	$h+2k=3n$ l : pair	$2f_0$	$4\gamma_{max} f_0^2$
NaCl Structural	$h+k+l=2n+1$	$4(f_{A'}+f_A)$	$16\gamma_{max}(f_{A'}+f_A)^2$
	$h+k+l=2n$	$4(f_{A'}-f_A)$	$16\gamma_{max}(f_{A'}-f_A)^2$
ZnS Structural	$h+k+l=2n+1$	$4(f_{A'}^2+f_A^2)^{\frac{1}{2}}$	$16\gamma_{max}(f_{A'}^2+f_A^2)$
	$h+k+l=2(2n+1)$	$4(f_{A'}-f_A)$	$16\gamma_{max}(f_{A'}-f_A)^2$
	$h+k+l=2.2n$	$4(f_{A'}+f_A)$	$16\gamma_{max}(f_{A'}+f_A)^2$

IV.9 **Experimental methods for the identification of crystalline structures**

Example of the XRD spectrum



We compare the formula for intensity I with the extinction conditions of Cs, CC, and CFC, then the hc……

The comparison table:

$I = f(2\theta_i)$	$\theta_i(°)$	$\sin^2(\theta_i)$	$1.\frac{\sin^2(\theta_i)}{\sin^2(\theta_1)}$	$2.\frac{\sin^2(\theta_i)}{\sin^2(\theta_1)}$	$3.\frac{\sin^2(\theta_i)}{\sin^2(\theta_1)}$	$h^2+k^2+l^2$			$n = h^2+k^2+l^2$	Plan (hkl)	a(Å)
						CS	CC	CFC			
						1	-	-	1	100	
						2	2	-	2	110	
						3	-	3	3	111	
						4	4	-	4	200	
						5	-	-	5	210	
						6	6	-	6	211	
						-	-	-	7	-	
						8	8	8	8	220	
						9	-	-	9	300 221	
						10	10	-	10	310	
						11	-	11	11	311	
						12	12	12	12	222	
						13	-	-	13	320	
						14	14	-	14	321	
						-	-	-	15	-	
						16	16	16	16	400	
						17	-	-	17	410	
						18	18	-	18	411 330	
						19	-	19	19	331	
						20	20	20	20	420	

We compare the indicated columns with those from the theory and take the values that are closest between the theoretical and the experimental. If we do not find any value identical to the CS, CC, or FCC structures, we look in the other structures (e.g., hc...).

Serie N^0 03 : (X-ray Diffraction)

Exercise 01

1. Recall the expressions of the structure factors of three monoatomic crystals whose Bravais lattices are respectively simple cubic, body-centered cubic, and face-centered cubic.

2. Calculate the structure factor of a crystal formed from a single type of atom and crystallizing in the diamond structure.

3. Calculate the structure factor of zinc with a blende structure.

4. Provide the first ten permitted reflections in each of the five cases.

5. Samples of powder from three different monoatomic cubic crystals are analyzed with a Debye-Scherrer camera. It is known that one of the samples is face-centered cubic, another is body-centered cubic, and the last one has a diamond structure. The approximate positions of the first four diffraction rings in some cases are given in the following table:

A	B	C
42.2°	28.8°	42.8°
49.2°	41.0°	73.2°
72.0°	50.8°	89.0°
87.32°	59.6°	115.0°

The values 2θ for samples A, B, and C.

a. Identify the crystal structures of A, B, and C.

b. If the wavelength of the incident X-ray beam is equal to 1.54 $\AA$, what is the length of the edge of the conventional cubic cell in each case?

Exercise 02

Part A: X-ray Diffractions

We perform a diffraction spectrum of a Silicon sample using an X-ray diffractometer. The wavelength used is equal to 1.54 $\AA$. We record the positions of the samples of the different

lines.

1. Complete the third row of the table.

2. We ask:

$$Q_i = \frac{4sin^2\theta_i}{\lambda^2}$$

- Complete the fourth row of the table

- 1. Assuming the cubic lattice, show that there exists a constant D, such that for all i:

$$\frac{Q_i}{D} = n$$

n is a natural integer that we will determine. Calculate the value of D.

- 2. Deduce the values of (hkl).

- 3. Specify the nature of the network and express the network parameter in the form $a \mp \Delta a$.

i	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
$\boldsymbol{2\theta_i}$(°)	28.4	47.3	55.9	68.8	76.0	87.6	94.5	106	113	127	136	156
$\boldsymbol{\theta_i}$(°)												
$\boldsymbol{Q_i = \frac{4sin^2\theta_i}{\lambda^2}}$												
$\boldsymbol{h^2 + k^2 + l^2}$												
(hkl)												

Part B: Electron Diffraction

In an experiment of fast electron diffraction by transmission, electrons accelerated by a d.d.p $U_0 = 30KV$ pass through a polycrystalline Silicon film of thickness e. we then observe diffraction rings on a photographic plate placed at a distance D from the film such that $e \ll D$

1. Calculate the wavelength of the incident electrons.

2. Calculate the structure factor of Silicon knowing that it crystallizes in the diamond structure with a lattice parameter $a = 5.43A°$..

3. Give the sequence of the first 6 allowed reflections for Silicon.

4. Deduce the corresponding distances$d_{(hkl)}$.

5. Calculate the first six values of the Bragg angles $\theta_{(hkl)}$.

6. Indicate $r_{(hkl)}$ the radii of the first six diffraction rings when $D = 30cm$.

Exercise 03: Study of the rutile structure

The structure of TiO_2 in the rutile form can be described as a compact hexagonal stacking of oxygen atoms in which one out of every two octahedral sites is regularly occupied by a titanium atom. We denote F_{T_i} and F_0 as the atomic form factors of titanium and oxygen, respectively. The coordinates of the atoms in the lattice are:

Titanium Ti: $(0,0,0)$; $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

Oxygen O: $(d,d,0)$; $(-d,-d,0)$; $\left(\frac{1}{2}-d,\frac{1}{2}+d,\frac{1}{2}\right)$, $\left(\frac{1}{2}+d,\frac{1}{2}-d,\frac{1}{2}\right)$, $(d \in R)$

1. Calculate the structure factor $F(h,k,l)$ of TiO_2.
2. Show that for any plane $(0,k,l)$ $F(0,k,l) = 0$ if and only if there exists a natural integer n such that $k + l = 2n + 1$.

Chapter IV: Chemical Bond

Introduction

Solid materials are made up of atoms (or ions) arranged in a crystalline structure. These atoms (or ions) are held together by electric forces that form chemical bonds. These bonds are entirely responsible for its mechanical, thermal, electrical, magnetic, ... properties. A solid can be considered as composed of an ionic core (nuclei + bound electrons) and valence electrons (electrons whose configuration in the solid may differ from that of the isolated atom).

2.9 Different types of crystals

The different types of bonds present in crystalline solids are mainly due to the different spatial distributions of valence electrons and ions that make up these solids. Crystalline solids can be classified into five types according to their bonds:

$$\left.\begin{matrix} -\ ionic\ bond\ crystals \\ -\ covalent\ bond\ crystals \\ -\ metallic\ bond\ crystals \end{matrix}\right\} \text{Strong ties}$$

$$\left.\begin{matrix} -\ \text{Van der Waals bonded crystals} \\ -\ c\text{hydrogen} - \text{bonded crystals} \end{matrix}\right\} \text{Weak ties}$$

2.10 Cohesion Energy

The cohesive energy of a crystalline solid is defined by the relation:

$$Cohesion\ Energy = E(crystal) - E(isolated\ atoms)$$

E(crystal): Total energy of the crystal

E (isolated atoms): Energy of infinitely distant atoms (therefore without interactions) To have a stable in a solid, the cohesive energy must be negative:

$$E_{Cohesion} < 0$$

2.11 The different types of crystals

2.11.1 **Ionic Crystals**

Ionic crystals are formed by the stacking of positively charged ions (cations) and negatively charged ions (anions). These crystals possess electronic charge distributions that are highly concentrated near the ionic cores.

As examples of ionic crystals, one can mention: Sodium chloride (NaCl), Potassium chloride (KCl), Cesium chloride (CsCl), …

Ionic crystals, whose bonding is ensured by the interaction between positive ions (cations) and negative ions (anions), are generally characterized by the following properties:
- Strong binding energy (or cohesion).

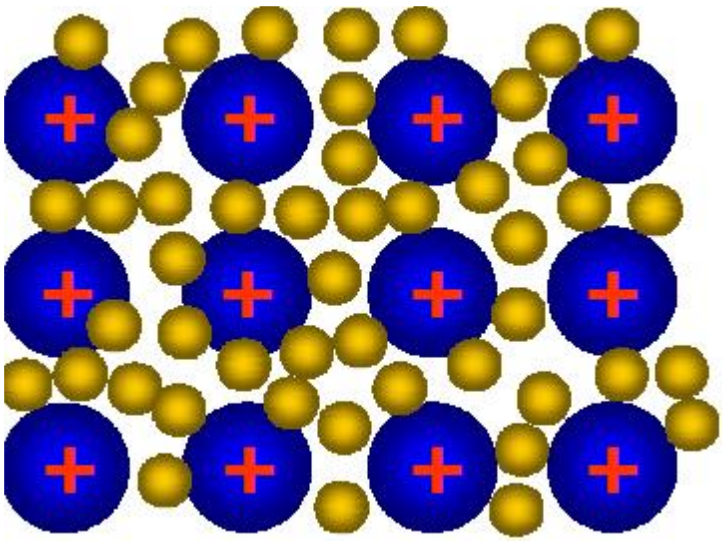
- High melting point.

- Low electrical conductivity.

- Low thermal conductivity.

2.11.2 **Metallic Crystals**

In a metal, the valence electrons of the atoms are delocalized throughout the crystal. These "free" electrons are called conduction electrons. The metallic bond is ensured by the interaction between ions and electrons.



Metal = a collection of positive ions + a "sea" of free electrons.

Metallic crystals, whose bonding is ensured by the interaction between ions and conduction electrons, are generally characterized by the following properties:

- High cohesion energy.
- High melting point.
- High electrical conductivity.
- High thermal conductivity.

2.11.3 **Covalent crystals**

Covalent crystals are materials where the electrons are not localized near the ionic cores. The electronic distribution is actually localized in a common region between neighboring atoms. This pooling of electron pairs between atoms gives rise to the covalent bond characterized by high energy.

The electrons in covalent bonds are generally immobile, so a covalent solid is a poor conductor. Carbon (graphite form or diamond form), semiconductors (Silicon, Germanium, …), and CH_4 are all covalent materials. Generally, covalent crystals are characterized by the following properties:

- Very high cohesion energy.
- High melting point.
- Low electrical conductivity.
- Low thermal conductivity.

(except for high-temperature semiconductors).

2.12 Van der Waals bonded crystals

Van der Waals bond crystals are rare gases except for helium (for which quantum effects play a crucial role). These molecular crystals (Neon, Argon, Krypton, Xenon) are composed of molecules that are little different from the individual isolated molecules. The electronic configuration of van der Waals crystals is of the stable full shell type (ns2np6) such as Neon (Ne), Argon (Ar), Krypton (Kr), and Xenon (Xe). In the solid state, Van der Waals crystals stack very densely and their crystal structures are face-centered cubic. They are generally characterized by the following properties:

- Very low cohesive energy
- Very low melting point
- Low electrical conductivity (insulators)
- Low thermal conductivity

2.13 Hydrogen Bonded Crystals

Hydrogen (H) has only one electron, it can only form a covalent bond with a single atom. However, there are cases where a hydrogen atom is attracted by two atoms at the same time: this is hydrogen bonding. This bond is characterized by a low energy: on the order of 0.1 eV. The hydrogen bond occurs between H and highly electronegative atoms: Fluorine (F), Oxygen (O), Nitrogen (Ne). Example The H2O molecule.

2.14 Cohesion energy in ionic crystals

The interaction energy between two ions i and j is given by:

$$U_{ij} = \mp\frac{q^2}{r_{ij}} + \lambda e^{\left(-\frac{r_{ij}}{\rho}\right)}$$

λ *and* ρ are parameters characterizing each ionic crystal.

$\frac{q^2}{r_{ij}}$: Electrostatic interaction term.

$\boldsymbol{\lambda e^{\left(\frac{r_{ij}}{\rho}\right)}}$ **:** Repulsion interaction term.

The total energy of a crystal composed of N molecules, or 2N ions, is given by:

$$U = \frac{1}{2}\sum_{i,j}^{2N} U_{ij} = \frac{1}{2}\sum_{i=1}^{2N}\left\{\sum_{i\neq j}\left[\lambda e^{\left(-\frac{r_{ij}}{\rho}\right)} \mp \frac{q^2}{r_{ij}}\right]\right\}$$

$$U = N\sum_{i\neq j}\left[\lambda e^{\left(-\frac{r_{ij}}{\rho}\right)} \mp \frac{q^2}{r_{ij}}\right]$$

Let r be the distance between the first nearest neighbor ions. All other distances can be expressed in terms of r. We set $r_{ij} = p_{ij}r$ and we write:

$$U = N\sum_{i\neq j}\left[\lambda e^{\left(-\frac{p_{ij}r}{\rho}\right)} \mp \frac{q^2}{r_{ij}}\right]$$

The repulsion (exponential term) converges quickly, we limit ourselves only to the Z nearest neighbors for this term.

The total energy of the crystal is then written as:

$$U(r) = N\sum_{i\neq j}\left[Z\lambda e^{\left(-\frac{r}{\rho}\right)} - \alpha\frac{q^2}{r}\right], \alpha = \sum_{i\neq j}\left[\frac{\mp 1}{p_{ij}}\right].$$

Where a is called the "Madelung constant."

Calculation of cohesive energy:

At the equilibrium distance r = r_0, the total energy is minimal:

$$\left(\frac{dU}{dr}\right)_{r=r_0} \mapsto Z\lambda e^{\left(-\frac{r_0}{\rho}\right)} = \alpha\rho\frac{q^2}{r_0}$$

The total energy at equilibrium (cohesion energy of the crystal) is then written as:

$$U(r_0) = -N\alpha\frac{q^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$$

The quantity $-N\alpha\frac{q^2}{r_0}$ is called "Madelung Energy."

2.15 Compression module

The compression (or compressibility) modulus B of a solid is defined by:

$$B = -V\frac{dP}{dV}$$

where V is the volume of the crystal and P is the applied pressure. Note that the compression is the inverse of the compression modulus. In the ground state, the differential of the internal energy reduces to the elementary pressure work, hence: $dU = -PdV$

$$B = -V\frac{d^2U}{dV^2}$$

B represents the energy required to produce a given deformation. The higher the B modulus, the more rigid the crystal.

2.16 Cohesion in Van der Waals crystals

2.16.1 Interaction potential between two atoms

In the case of Van der Waals bonded crystals, the interactions between atoms are very weak. The potential interaction between two atoms separated by a distance r can be written as:

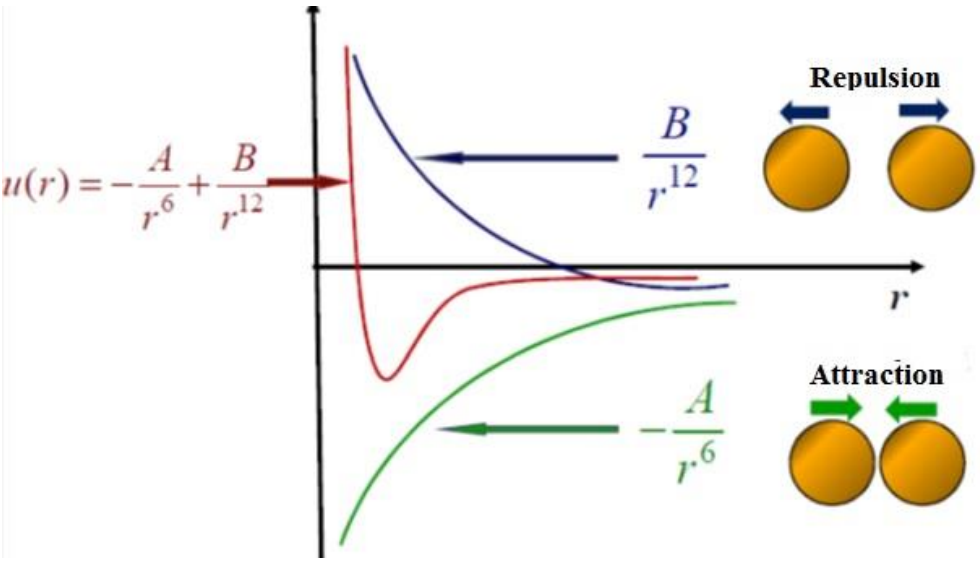
$$U(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

where A and B are positive constants determined experimentally in the gas phase. This interaction energy is composed of two contributions:

$-\frac{A}{r^6}$: Attractive interaction potential (negative term).

$\frac{B}{r^{12}}$ ：Repulsive interaction potential (positive term).

The following figure shows the graphical representation of the interaction potential.



Serie N° 4: Chemical Bond

Exercise 1:

The cohesive energy of two atoms separated by a distance R in a given molecule is given by the following expression: $U_{TOt}(R) = -\frac{\alpha}{R} + \frac{\beta}{R^8}$ such that α and β are constants.

1- Calculate R_0 at equilibrium as a function of α and β.

2- Calculate the ratio between the attraction and repulsion energies at equilibrium.

3- If $R_0 = 2.8A°$ and the binding energy $U_{TOt}(R) = 5eV$, what are the values of α and β and what is the force required to reduce the distance between the atoms by 5%.

Exercise 2:

Using the Lennard-Jones potential, show that the cohesive energy of an atom in a rare gas crystal in the C.F.C structure is less than that in the S.C or C.C structure.

We give:

C.F.C	C.F.C	S.C	C.C
A_6 :	14.45	8.40	12.25
A_{12} :	**12.13**	**6.20**	**9.11**

Exercise 3:

The potential energy of attraction between two rare gas atoms (van der Waals), separated by a distance r, is of the form A/r^6, while the repulsive energy due to the overlap of electronic orbitals is of the form B/r^{12}. However, the Lennard-Jones energy is usually expressed in the form: $U = 4\varepsilon\,[(\frac{\sigma}{r})12 - (\frac{\sigma}{r})6]$.

1- By expressing A and B in terms of ε and show that the two expressions are equivalent.

2- Extract the physical meaning of the parameters ε and σ by expressing the distance r_0 separating two atoms at equilibrium as a function of as well as the resulting cohesive energy as a function of ε.

3- The Bravais lattice of rare gas crystals is f.c.c with lattice parameters:

a = 4.46Å (Ne); a = 5.31Å (Ar); a = 5.64Å (Kr); a = 6.13Å (Xe),

while their cohesive energies are respectively 20 meV (Ne), 80 meV (Ar), 116 meV (Kr), and 170 meV (Xe). Deduce the numerical values of σ and ε.

Exercise 4:

List the forces that bind atoms together and briefly enumerate a few examples.

The interaction potential between two atoms of a molecule separated by a distance r is given by:

$$U(r) = -\frac{A}{r^m} + \frac{B}{r^n}$$

What do these terms mean? Deduce the minimum potential and say what consequences can be drawn from it.

A uniaxial chain of N anions and N cations separated by a distance r (see the following diagram).

Show that the internal energy (Coulomb interaction) is given by the following expression:

$$U(r) = \sum 2NK \frac{e^2(-1)^{n+1}}{n+1}, \text{ n} \geq 0$$

Exercise 05:

1. Calculate the electrostatic potential energy Up of an ion in the following two cases:
- Linear ionic chain

- Cubic aggregate of 8 ions.

Deduce the expression for α and give the physical significance of this energy of the form

$$U(r) = -\frac{\alpha q^2}{4\pi r \varepsilon_0}$$

2. It is assumed that there is another interaction energy between two first neighbor ions of the form. what does this energy mean and plot the evolution of Up and Ur as a function of r. deduce that there is an equilibrium position r0 and demonstrate that the cohesion energy Uc given by:

$$U_c = -\frac{\alpha q^2}{4\pi r \varepsilon_0}(1 - \frac{1}{p})$$

Calculate the values of α for the two structures (we will take $p = 9$, $r_0 = 2.8$ Å, 1st PV, 2nd, 3rd PV.

3. It is assumed that $U_r = \lambda e^{-r/\rho}$. Provide the new expression of U_c. Calculate the compressibility modulus of the crystal $B = -V(\frac{dP}{dV})$ or $P = -(\frac{dU}{dV})$. V: the volume of the unit cell (for $U_r = \lambda e^{-r/\rho}$).

Chapter V: Vibrations and Heat Capacity

Introduction

We saw in the previous chapters that atoms organizes themselves in crystals to form well-defined crystalline structures. The temperature being zero and the atoms are fixed in their equilibrium positions.

If we now place ourselves at a temperature different from zero, the atoms of the crystal are thermally excited and will vibrate around their equilibrium positions. The energy of such a vibration is quantized, and the energy quantum is called a phonon, by analogy with the photon of an electromagnetic wave.

3.1 Notion of phonon

The phonon is a concept in quantum mechanics that invokes the idea of wave-particle duality (as is the case with photons). According to this concept, the phonon can manifest either as a wave (elastic wave) or as an elementary packet (or quantum).
If the study of phonons plays a significant role in condensed matter physics, it is because they play an important role in a large number of physical properties of materials, including heat capacity, thermal conductivity, and electrical conductivity.

3.2 Heat capacity

The heat capacity (or thermal capacity) at constant volume of a substance is a quantity defined based on its internal energy U, that is to say, its total energy when the body is macroscopically at rest and subjected to no external action:

$$C_V = \left(-\frac{\partial U}{\partial T}\right)_V$$

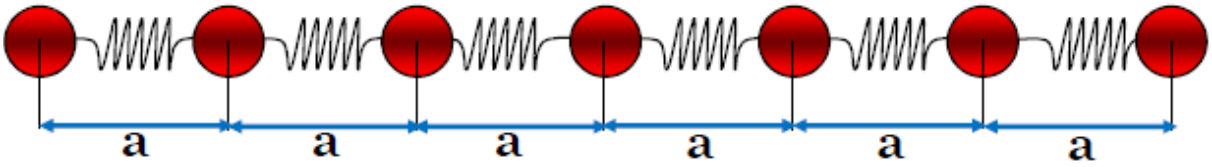
C_V is expressed in joules per kelvin (J/K).

Heat capacity is an extensive property: the greater the amount of substance, the greater the heat capacity.

3.3 Vibration of a monoatomic chain

We consider an atomic chain composed of identical atoms of mass m. It is a one-dimensional crystal with a lattice parameter a. Under the action of the temperature T, the atoms in this chain vibrate and undergo displacements from their equilibrium positions. It is assumed that these displacements occur parallel to the direction of the chain and that they are small compared to the interatomic distances. This allows the crystal to be treated using a simple theory: "the harmonic approximation."

In this approximation, the vibrations of the atoms are treated as harmonic oscillators.

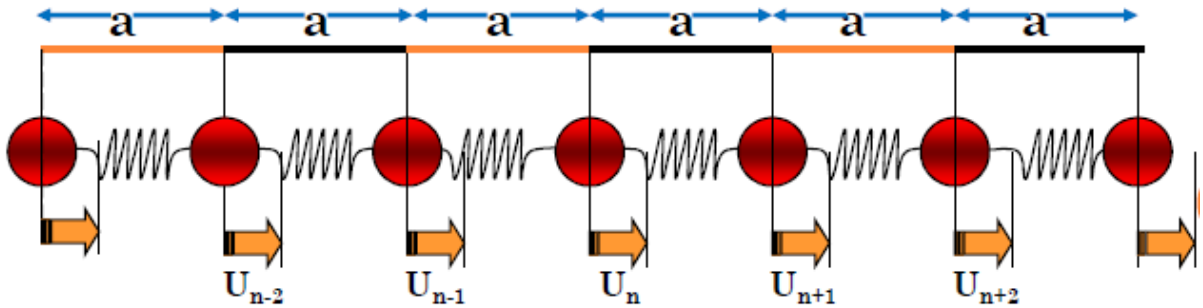


3.3.1 Equation of motion

Let the displacement of the n-th atom relative to its equilibrium position be denoted. This atom is subjected to the action of all the atoms p ($p \neq n$). The resultant force Fn exerted on the atom with index n can be written as:

$$F_n = \sum_{p \neq n} C_p (U_{n+1} - U_n)$$

where Cp is the recall constant between atom n and atom n + p, with (Cp = C-p).



$$F_n = C(U_{n+1} + U_{n-1} - 2U_n$$

where C is the spring constant between nearest neighbor atoms.

Newton's second law translates to:

$$m\ddot{U} = C(U_{n+1} + U_{n-1} - 2U_n$$

It is a second-order linear differential equation. It admits plane wave solutions with amplitude u_0 and wave vector K:

$$U_n = U_0 e^{i(x_n K - \omega t)} = U_0 e^{i(naK - \omega t)}$$

a being the network parameter and ω the wave frequency.

3.3.2 Dispersion Relation

By holding both previous expressions, we obtain:

$$m\omega^2 = -C(e^{iKa} + e^{-iKa} - 2)$$

$$m\omega^2 = 2C(1 - cosKa)$$

According to trigonometric relations, we obtain:

$$\omega^2 = \frac{4C}{m} sin^2(\frac{Ka}{2})$$

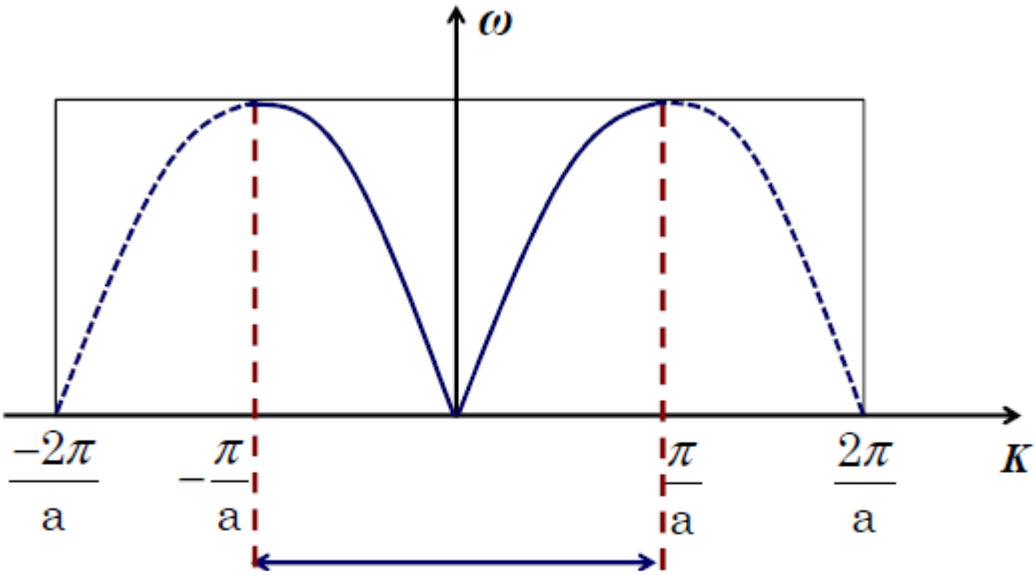
So,

$$\omega = \sqrt{\frac{4C}{m}} sin(\frac{Ka}{2})$$

This relationship is called the phonon dispersion relation. In the first Brillouin zone, the values of K range between

$$\frac{\pi}{a} < K < \frac{\pi}{a}$$

In the following figure, we have represented the dispersion relation ω = f(K) of the monoatomic chain.



First Brillouin Zone

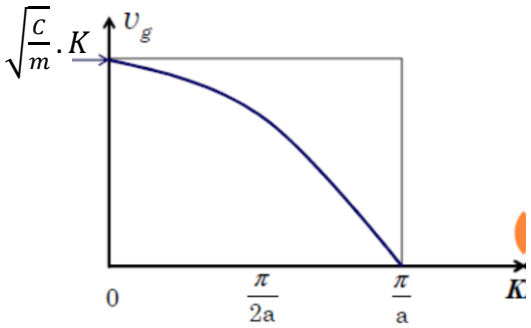
3.3.3 Group speed

Given a wave packet that propagates through the network. The speed of this wave packet is called the group velocity and is defined by:

$$v_g = \frac{d\omega}{dK}$$

The group velocity represents the speed of energy transmission in the medium. In the case of the atomic chain, we obtain:

$$v_g = \sqrt{\frac{Ca^2}{m}}.cos\frac{Ka}{2}$$



In the case of long wavelengths, we have:

$$Ka \ll 1 \text{ et } sin\frac{Ka}{2} \approx \frac{Ka}{2}$$

and the dispersion relation becomes:

$$\omega = \sqrt{\frac{C}{m}}.Ka$$

It is a linear relationship between the frequency and the wave vector. In this case, the group velocity is referred to as the sound speed vs and is written as:

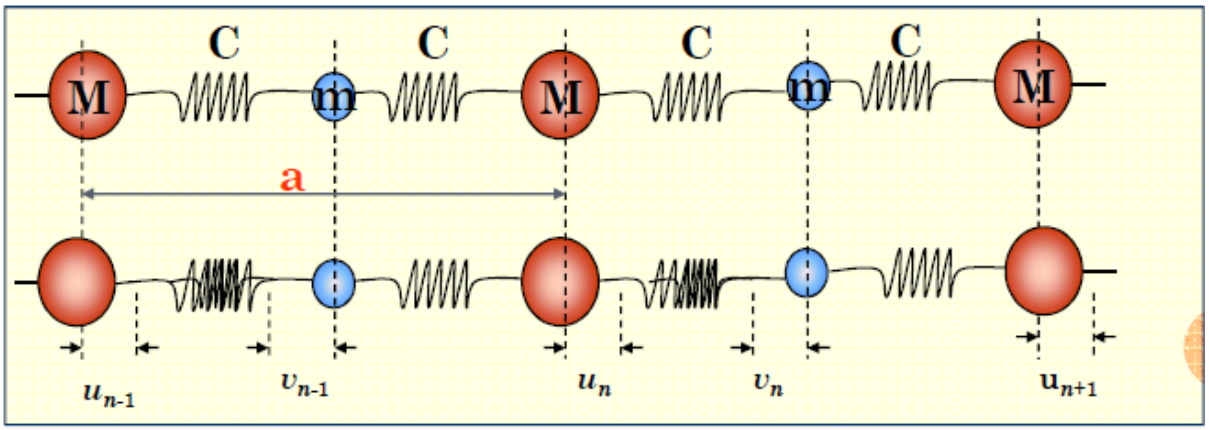
$$v_g = \sqrt{\frac{C}{m}}a$$

This speed is independent of frequency, exactly like in the case of elastic waves in a continuum.

3.4 Vibration of a chain atomic

3.4.1 Equation of motion

Consider a diatomic chain, with a lattice parameter a, consisting of two atoms with respective masses M and m. We assume that each atom interacts with its nearest neighbors with the same spring constant C, denoting u as the displacement of the atom with mass M and v as the displacement of the atom with mass m.



As in the case, the equations of motion for the two types of atoms are written as:

$$m\ddot{u} = C(v_{n+1} + v_{n-1} - 2u_n)$$

$$m\ddot{v} = C(u_{n+1} + u_{n-1} - 2v_n)$$

We will look for solutions having the wave propagation form of amplitudes *u* and *v*.

$$u_n = u_0 e^{i(naK-\omega t)}$$

$$v_n = v_0 e^{i(naK-\omega t)}$$

By substituting these relations into the equations of motion, we obtain:

$$-\omega^2 Mu = Cv\left(1 + e^{-iKa}\right) - 2Cu$$

$$-\omega^2 mv = Cu\left(1 + e^{iKa}\right) - 2Cv$$

The system of homogeneous linear equations with two unknowns u and v has non-trivial solutions only if the determinant of the system is zero:

$$\begin{vmatrix} 2C - M\omega^2 & -C(1 + e^{-iKa}) \\ -C(1 + e^{iKa} & 2C - m\omega^2 \end{vmatrix} = 0$$

We then obtain a biquadratic equation:

$$Mm\omega^4 - 2C(M + m)\omega^2 + 2C^2(1 - cosKa) = 0$$

The solution of this equation in ω2 gives:

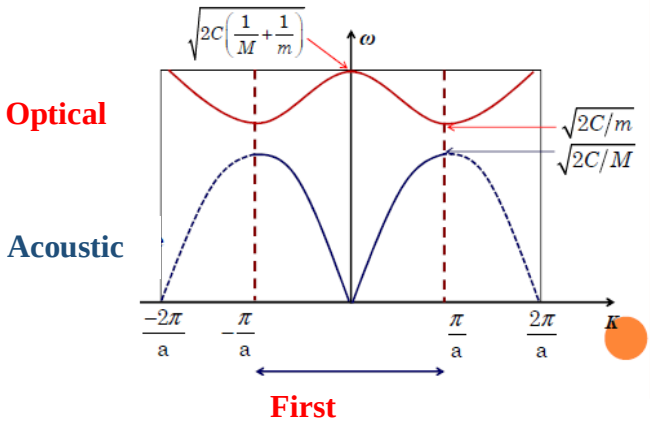
$$\omega^2 = C\left(\frac{1}{M} + \frac{1}{m}\right) \mp C\sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} sin^2 \frac{Ka}{2}}$$

3.4.2 Dispersion relation

i) The expression of ω_ with the plus sign translates to a dispersion relation known as the "optical branch." For large wavelengths (Ka << 1), we obtain:

$$\omega^2 \cong 2C\left(\frac{1}{M} + \frac{1}{m}\right)$$

In the vicinity of 0, the group velocity is constant and equal to the speed of sound.



3.5 Einstein Model for Heat Capacity

3.5.1 Internal energy

In 1900, Max Planck introduced the concept of quantization for the first time to explain the electromagnetic spectrum of black body radiation. This idea was taken up by Einstein in 1907 to describe the contribution of lattice vibrations to the heat capacity of a crystalline solid. It is based on the following assumptions:

Each atom in the structure is a 3D quantum harmonic oscillator,

The atoms vibrate at the same frequency, unlike the Debye model.

• The energy of a one-dimensional oscillator (proposed by Planck in 1900) is expressed as:

$$E_n = nh\omega$$

If the crystal is composed of N atoms, its internal energy U is obtained by calculating the average energy of the N three-dimensional quantum harmonic oscillators. Einstein considers that the atoms of the crystal vibrate at the same frequency, called the Einstein frequency and denoted as ω_E. This hypothesis leads to rewriting the internal energy in the form:

$$U = 3N\bar{E} = 3N\frac{h\omega_E}{exp^{\beta h\omega_E} - 1}$$

Demonstration

We calculate the partition function of a quantum harmonic oscillator, which is given by the relation:

$Z = \sum_{i=0}^{\infty} exp^{-\beta E_n}$ avec $\beta = \frac{1}{K_B T}$

where K_B is the Boltzmann constant, T is the absolute temperature, and i is a state of the oscillator. There is only one state per energy level; the sum thus becomes:

$$Z = \sum_{n=0}^{\infty} exp^{-\beta E_n} = \sum_{n=0}^{\infty} exp^{-\beta nh\omega} = \sum_{i=0}^{\infty} exp^{(-\beta h\omega)^n}$$

By applying the formula for the sum of a geometric series, we simplify the partition function:

$$Z = \frac{1}{1 - exp^{-\beta h\omega}}$$

We then obtain the energy of an oscillator:

$$\bar{E} = -\frac{\partial LnZ}{\partial \beta}$$

With what it gives

$$\bar{E} = \frac{h\omega}{exp^{\beta h\omega} - 1}$$

The internal energy of the system is then:

$$U = 3N\bar{E} = 3N\frac{h\omega}{exp^{\beta h\omega} - 1}$$

3.5.2 Heat capacity

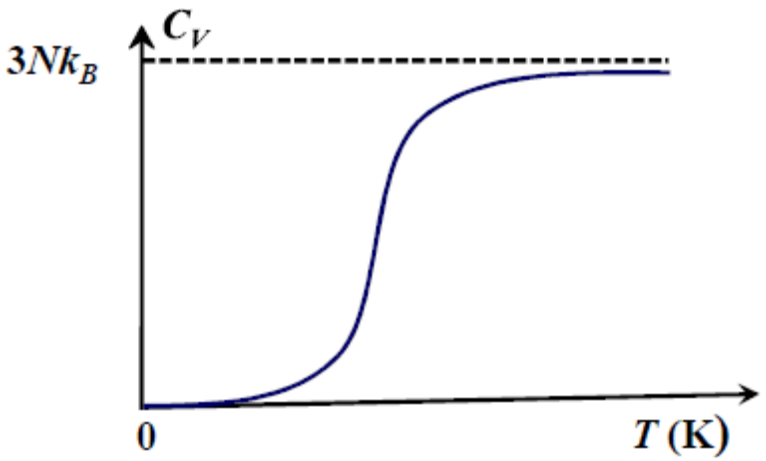
The heat capacity at constant volume is obtained by differentiating the internal energy U with respect to the temperature *T*:

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B(\beta h\omega_E)^2 \frac{\exp(\beta h\omega_E)}{[\exp(\beta h\omega_E) - 1]^2}$$

One can define Einstein's temperature as $\theta_D = \frac{h\omega_E}{k_B}$ and we write:

$$C_V(T) = 3Nk_B(\frac{\theta_E}{T})^2 \frac{\exp(\frac{\theta_E}{T})}{\left[\exp\left(\frac{\theta_E}{T}\right) - 1\right]^2}$$

The shape of the C_V (T) curve is shown in the following figure:



For high temperatures $T \gg \theta_E$, we obtain:

$$C_V \approx 3Nk_B$$

This result is analogous to the empirical law of Dulong and Petit obtained in 1819 by measuring the heat capacity of crystalline solids at sufficiently high temperatures. For low temperatures $T \ll \theta_E$, we obtain:

$$C_V = 3Nk_B(\frac{\theta_E}{T})^2 \exp(-\frac{\theta_E}{T})$$

This result is less consistent with experimental measurements. Indeed, experiments show that the heat capacity of crystal lattices depends on T^3 at low temperatures, which is not the case for the Einstein model. This discrepancy with the experiment can be explained by Einstein's hypothesis that harmonic oscillators vibrate at the same frequency.

3.5.3 General formulation of heat capacity

3.5.3.1 General expression of internal energy

We consider a crystal as a set of identical harmonic oscillators in thermal equilibrium. To establish an accurate expression for the internal vibrational energy U of this crystal, it is necessary to take into account that the phonons vibrate at different frequencies. U can be written in the form:

$$U = \sum_k^k \bar{n}h\omega = \sum_k \frac{h\omega_k}{exp^{\beta h\omega_k} - 1}$$

Where $\bar{n} = \frac{1}{exp^{\beta h\omega_{k-1}}}$ the Bose-Einstein distribution

It is more interesting to replace the discrete sum with an integral. For this, we will introduce the density of oscillation frequencies $D(\omega)$, called the mode density. U can be rewritten as:

$$U = \int_0^\infty D(\omega)\bar{n}h\omega\, d\omega = \int_0^\infty D(\omega)\frac{h\omega_k}{exp^{\beta h\omega_k} - 1}d\omega$$

3.5.3.1.1 One-dimensional mode density

Let's consider the problem of the vibrations of a row of length L containing N atoms separated by a. Let there be an elastic wave that propagates along this row. The boundary conditions are ensured by the Born von Karman cyclic conditions:

$$u(x_n + L) = u(x_n) \Rightarrow u_0 e^{i\left((x_n+L)k-\omega t\right)} = u_0 e^{i(x_n k-\omega t)}$$

$$\Rightarrow e^{ikL} = 1$$

The allowed values of K are: $K = 0, \mp\frac{2\pi}{L}, \mp\frac{4\pi}{L}, \mp\frac{6\pi}{L}$…….

Two successive values of K are separated by an interval:

$$\Delta K = \frac{2\pi}{L}$$

Let *dN(K)* be the number of K contained in the interval *[K, K+dK]*. *dN(K)* is given by:

$$dN(K) = \frac{2dK}{\frac{2\pi}{L}} = \frac{L}{\pi}dK$$

The density of K is given by: $D(K) = \frac{dN(K)}{dK} = \frac{L}{\pi}$

Since we are looking for the mode density (or frequency density) $D(\omega)$, we can write:

$$D(K)dK = D(\omega)d\omega \Rightarrow D(\omega) = \frac{L}{\pi}\frac{dK}{d\omega} = \frac{L}{\pi}\frac{1}{v_g}$$

3.5.3.1.2 Three-dimensional mode density

We now consider, for example, a cubic sample with a side length of L. The periodic boundary conditions of Born von Karman are written as:

$$u(x_n + L, y_n, z_n) = u(x_n, y_n, z_n)$$

$$u(x_n, y_n + L, z_n) = u(x_n, y_n, z_n)$$

$$u(x_n, y_n, z_n + L) = u(x_n, y_n, z_n)$$

The allowed values of K (K_x, K_y, K_z) are:

$$K_x, K_y, K_z = 0, \mp\frac{2\pi}{L}, \mp\frac{4\pi}{L}, \mp\frac{6\pi}{L}$$

A permissible value of K occupies a volume equal to $(\frac{2\pi}{L})^3$

The number of modes N(K) whose wave vector is less than K is the ratio between the volume of the sphere of radius K and the volume occupied by a K:

$$N(K) = \frac{4\pi K^3/3}{(\frac{2\pi}{L})^3} = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi K^3}{3} = \frac{V}{2\pi^2}\frac{K^3}{3}$$

where V = L3 is the volume of the crystal.

The density of states D(ω) for a phonon wave polarization is given by:

$$D(\omega) = \frac{dN(K)}{d\omega} = \frac{dN(K)}{dK}\frac{dK}{d\omega} = \frac{VK^2}{2\pi^2}\frac{dK}{d\omega}$$

To obtain the final expression of $D(\omega)$, the dispersion relation $\omega = f(K)$ must be known.

3.6 Debye Model for Heat Capacity

3.6.1 Density of states in the Debye model

In 1912, Debye proposed a model for heat capacity in which the dispersion relation is written as: $\omega = vK$, v: Speed of sound.

The density of states for each polarization takes the form:

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3}$$

If there are N elementary cells in the sample, the total number of acoustic phonon modes is N. We define a cutoff frequency ω_D called the Debye frequency by:

$$\int_0^{\omega_D} D(\omega)d\omega = N \Rightarrow \omega_D^3 = \frac{6\pi^2 v^3 N}{V}$$

N= 1 for 1D and N= 3N for 3D.

In the Debye model, the frequencies of vibrations greater than ω_D are not allowed.

3.6.2 Internal energy

During an atomic vibration, the wave propagates either longitudinally or transversely relative to the direction of propagation. Three polarizations can occur: one longitudinal wave and two transverse waves. For each type of polarization, the internal energy U is written as:

$$U = \int_0^{\omega_D} D(\omega)\bar{n}h\omega d\omega = \int_0^{\omega_D} (\frac{V\omega^2}{2\pi^2 v^3}) \frac{h\omega}{exp^{\beta h\omega} - 1} d\omega$$

We assume that the speed of phonons is independent of polarization. To obtain the total internal energy of the crystal, the previous relation of U must be multiplied by 3, and we get:

$$U = 3(\frac{hV}{2\pi^2 v^3}) \int_0^{\omega_D} \frac{\omega^3}{exp^{\beta h\omega} - 1} d\omega$$

The Debye temperature is defined by the relation $\theta_D = {h\omega_D}/{k_B}$

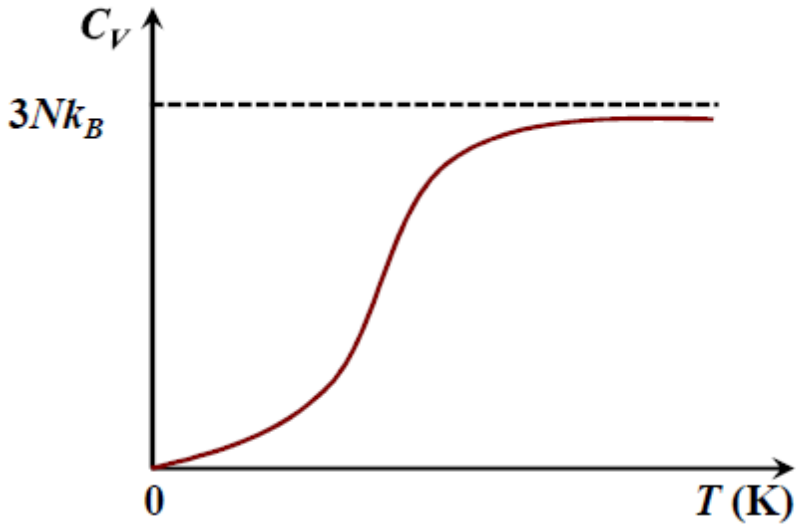
By asking $x = \beta h\omega$, $x_D = \beta h\omega_D = {\theta_D}/{T}$, we obtain:

$$U = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3}{(e^x - 1)} dx$$

By differentiating this expression with respect to temperature, we obtain the heat capacity of the crystal:

$$C_V(T) = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2} dx$$

We will represent the graphical appearance of C_V (T) and analyze the high and low temperature limits. The Debye heat capacity is represented in the following figure:



For high temperatures $T \gg \theta_D$ We obtain:

$$C_V = 3Nk_B$$

We find the empirical law of **Dulong and Petit**.

At very low temperatures, the upper limit of the integral can stretch towards infinity, and the obtained integral has the value:

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x-1)^2} dx = \frac{4\pi^4}{15}$$

Thus, the heat capacity takes the following form:

$$C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$$

As can be seen, Debye's heat capacity follows a T^3 law for low temperatures. This result is in good agreement with the experimental measurements.

Series N°5: Phonons

Exercise 01: Monoatomic

We consider a linear chain consisting of N identical atoms of mass m, equidistant by a, subjected to the constant β between nearest neighbors. We consider the Hook approximation

and limit ourselves to interactions between nearest neighbors.

1. Provide the equation of motion for the atom with index n for vibrations likely to propagate along the atomic chain in the form:

$$U_n = Ae^{i(\omega t - Kx_n)}$$

2. Establish the dispersion relation ω(k).
3. Determine the speed of sound V_S and the maximum frequency of atomic vibration γ_m.
4. By applying periodic boundary conditions, determine the density of states in k-space, g(k).
5. In the Debye approximation, determine the density of states in the frequency space g(ω) and in the frequency space.
6. Determine the Debye frequency γ_D and say if the Debye approximation is verified in our case (we will compare γ_D to $\gamma_m$which will be given as a function of V_S and a).
7. Provide the expression for the internal energy U due to lattice vibrations in integral form.
8. Give the expression of the specific heat C_V in integral form. Deduce its expression at high temperature ($KT >> h\gamma_D$).
9. Give the expression for U and that of CV as a function of the Debye temperature θ_D defined by: $h\gamma_D = K\theta_D$ at low temperature ($KT << h\gamma_D$). We give $\int_0^\infty \frac{x\,dx}{e^x-1} = \frac{\pi^2}{6}$.

Exercise 02: Diatomic

We consider a row of N pairs of atoms with masses m_1 and m_2 ($m_2 > m_1$) equidistant from R_0 at equilibrium. The interactions between a given atom and its nearest neighbors are characterized by the force constant β. The vibrations likely to propagate along the row are of the form:

$$U_n = Ae^{i(\omega t - K\overrightarrow{r_n})}$$

Where $\overrightarrow{r_n}$ is the instantaneous position of the atom with index n, relative to the origin located on one of the atoms, the average position of the atoms of mass m_1 is $2nR_0$. We are using Hook's approximation and the harmonic approximation.

1. What do these two approximations consist of? What is then the expression of ($\overrightarrow{r_n}$) and that of the vibrations of the two types of atoms?
2. Provide the equations of motion for the two types of atoms.
3. Knowing that the dispersion relation is of the form:

$$\omega^2 = \beta\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \mp \beta\left[\left(\frac{1}{m_1} + \frac{1}{m_2}\right)^2 - \frac{4sin^2 KR_0}{m_1 m_2}\right]^{1/2}$$

4. Provide the characteristic frequencies at the center and the edge of the Brillouin zone for the Acoustic Branches (AB) and the Optical Branches (OB). Subsequently, the dispersion relation of longitudinal acoustic phonons is assimilated to the Debye model; $\omega = V_S K$ and the dispersion relation of longitudinal optical phonons to the Einstein model with

$$\gamma_{Optique} = \gamma_E = Cste$$

5. Graphically represent the dispersion relations of BA and BO.
6. Determine the density of states in the k-space, g(k), and in the frequency space, g(γ).
7. Determine the specific heat C_{VA} associated with the BA at high and low temperatures as a function of the Debye temperature θ_D given by: $h\gamma_D = K\theta_D$where γ_D is the Debye frequency, we have: $$\int_0^\infty \frac{x\,dx}{e^x - 1} = \frac{\pi^2}{6}.$$
8. Same question for the specific heat C_{VO} associated with the BO as a function of the Einstein temperature θ_E given by: hγ_ $h\gamma_E = K\theta_E$.
9. At T=20K°, evaluate the specific heat of the crystal per atom pair, and conclude regarding the contribution of optical phonons and acoustic phonons. We are given:

R_0 = 3A°, $\gamma_E = 9{,}5.10^{12}\frac{}{S}, et\ V_S = 8800\frac{m}{S}, h = 6{,}6.10^{-34}\ J.S\ et\ K = 1{,}38.10^{-23}$ J/K.

References

[1]. 1987 عزيز عقيل داخل. مقدمة في فيزياء الجسم الصلب. ديوان المطبوعات الجامعية. الجزائر

[2] C. Jacques. Initiation à la physique du solide : exercices commentés. Masson, 1981.

[3]. C. Jacques. Understanding Solid State Physics: Problems and Solutions. CRC Press, 2016.

[4] N. W. Ashcroft and N. D Mermin. Edition original. Solid State Physics. Saunders College Publishing, 1976.

[5] K. Charles. Physique de d'état solide 5 ème Edition. Dunod université.

[6] K. Charles. Introduction to Solid State Physics Solution Manual. 2021.